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Effect of the Phase Transition of Ammonium Nitrate on the Storage Behaviour of Calcium Ammonium Nitrate

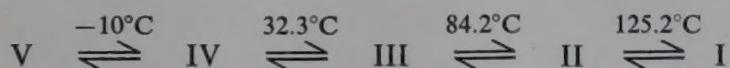
By

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Deterioration of calcium ammonium nitrate during its storage and transportation is a common occurrence under our climatic conditions. One of the causes is the phase change of ammonium nitrate between forms IV and III around 32°C. The transition temperatures of the above phase change of ammonium nitrate as well as of the diluted product have been determined with the help of a dilatometric technique. The influence of various additives on the transition temperature has been studied. Stability of granules towards "transition damage" has been determined and it has been found that the former depends on the size of the granules—smaller granules being stabler than the larger ones. The addition of ammonium sulphate to calcium ammonium nitrate increases its stability considerably.

Ammonium nitrate is known to undergo four phase transitions involving five stable crystalline modifications in the temperature range -20°C to its melting point 169°C. The transition temperatures¹ are as follows:



The transition between forms IV and III occurs around 32°C, which falls in the ambient range of temperature and is known to have an adverse effect on the keeping quality of ammonium nitrate. This transition has, therefore, attracted much attention in recent years and several interesting features have come to light^{2,3}. The specific volume increases during the upward transition IV→III, which is found to occur normally at a temperature higher than 32.3°C. The downward transition is attended by a decrease in the specific volume and occurs at a temperature lower than 32.3°C.

Lowry⁴ et al were first to discover hard caking in ammonium nitrate by the passage of the moist salt through the transition temperature between crystal forms IV and III. Whetstone⁵ attributed hard caking from phase transition to the difference in solubility between the stable and meta-stable forms of the salt. One of the present authors⁶ found that moist samples

of ammonium nitrate caked badly when temperature conditions were favourable for upward transition. The phase transition is known to affect granules, prills or crystals of ammonium nitrate in another way. These particles tend to swell, crack and finally disintegrate when subjected repeatedly to the variation in temperature around the transition temperature⁴. Loss of granular structure is a serious problem as ammonium nitrate in the form of powder forms an extremely hard cake. Disintegration of the prills in a dry blended mixture, recently observed during transportation of the fertilizer in USA., was found to be due to the phase transition⁷. Pure ammonium nitrate prills are known to start disintegrating only after six to ten cycles.

The efforts, made so far to prevent the rapid deterioration of ammonium nitrate fertilizer due to phase transitions during its storage and transportation, have mainly been directed towards shifting the transition temperature below or above the ambient temperature range. Effective lowering of the transition temperature has been successfully achieved by the addition of potassium nitrate to ammonium nitrate fertilizer. The extent of lowering is found to be dependent on the amount of potassium nitrate added—6°C for each per cent of potassium

nitrate⁸. Phase III of ammonium nitrate is stabilized at a lower temperature by forming a solid solution with potassium nitrate⁹. 2-5 per cent of potassium nitrate is considered sufficient for the purpose^{10,11}. Magnesium oxide when added to the molten mass of ammonium nitrate to the extent of 1 per cent has been claimed to be effective in increasing the transition temperature to about 50°C and thus shifting the phase transition above the ambient range of temperature. The presence of magnesium nitrate, however, has been found to make the fertilizer considerably more hygroscopic¹².

The problem has also been approached from a different angle, and attempts have been made to increase the stability of the fertilizer towards what may be termed as "transition damage". It has been reported that spraying of a molten mix of 50-85 per cent of ammonium nitrate with 50-15 per cent of mono-ammonium phosphate through the prilling tower produced extremely stable prills which did not deteriorate even after subjecting them to over 100 cycles over the temperature range 20-40°C¹³. A mixture of 0.5 per cent boric acid, 1 per cent diammonium phosphate and 0.05 per cent ammonium sulphate has also been claimed to be effective in preventing disintegration of ammonium nitrate at the III \rightleftharpoons IV transition as well as reducing the recycle fines in the manufacturing process from 8.5 to 1.3 per cent¹⁴. Recently researches by Vincent J. Russo* have revealed that certain nucleating agents (identity not disclosed) when added to ammonium nitrate modify the crystal habit from the large stressed crystals to the fine-grained ones with a considerable increase in the stability of the prills. The stabilized prills are stated to reduce product recycle fines thereby increasing the plant capacity by approximately 20 per cent¹².

Loss of granular structure of calcium ammonium nitrate (CAN) during its storage and transportation is quite common under our climatic conditions where temperature fluctuations often include the IV \rightleftharpoons III transition temperature of ammonium nitrate. Swelling and disintegration of CAN granules have been noticed on the top layer (2-4 cm. deep) in the bulk pile of the CAN storage silos at the two plants in India producing this fertilizer. The work described in the present communication has been undertaken to obtain further information on the effect of phase transition on the fertilizers with special reference to CAN. The effects of various additives on the stability and transition

temperature of ammonium nitrate and CAN have been studied with the help of dilatometric techniques.

Experimental

A known amount of ammonium nitrate was taken and dissolved in water. The diluent or an additive was then added. The solution was evaporated on a water-bath till a pasty mass was obtained. This mass was then transferred to a paddle-type granulator, and the granules obtained were sieved to get the required size. The oversize granules were broken to the required size and fines were rejected. The granules were then placed in a desiccator containing concentrated sulphuric acid for drying, after which the desired amount of moisture (0.5 per cent) was allowed to be absorbed by the granules. The samples were immediately used for the experiment to avoid any possible changes in moisture and temperature.

A simple dilatometric technique was employed to measure the transition temperature during the present study. The dilatometer consisted of a standard B-24 joint, the lower end of which was sealed and the upper end cut about 2 cm. from the joint and a graduated capillary fused to it. Two hooks were also attached to both the parts of the joint to fix springs between them to keep the joint tightly closed. Turpentine oil was used as a dilatometric liquid. Initially about half the tube was kept filled with the oil and then 10 g. of the sample were added slowly to it so that there are no air gaps in-between the granules. The whole of the tube was then placed in a turpentine bath and the joint fixed so that the level of the oil rises in the capillary. It was then removed, springs fixed in the hooks and allowed to stand at room temperature (30°C) for 4-5 hours, in a water bath such that the joint is just above the water level. At the time of experiment the bath temperature was gradually raised at the rate of 1/4 degree/min. and the oil level noted in the capillary. Normally, the oil-level rises regularly for each degree rise of temperature except at the transition temperature (Table 1) of the enclosed sample when there is an abrupt rise in the oil level over a range of 2-3 degrees.

Results

The results (Table 1) show that the transition temperature of pure ammonium nitrate as well as of most of the other samples is around 36°C which is higher than the quoted value 32.30°C. This is in accord with the results of Brown and McLaren², who using DTA found the transition temperature to be at 37°C. The nitrates of calcium and magnesium do not increase the transition

* A paper has subsequently appeared in the Indus. Engng. Chem. Product. Res. & Dev. Vol. 7(1) (1968), 69 by Russo in which aluminium silicate with and without metal oxides have been used as a nucleating agent.

TABLE 1—EFFECT OF ADDITIVES ON THE TRANSITION TEMPERATURE OF AMMONIUM NITRATE IV→III

Sample	Transition Temperature (Tc), °C IV→III
1. Ammonium Nitrate	36
2. Ammonium Nitrate +2% KNO ₃	No Expansion
3. Ammonium Nitrate +2% KCl	No Expansion
4. Ammonium Nitrate +2% K ₂ Cr ₂ O ₇	No Expansion
5. Ammonium Nitrate +2% FeSO ₄ (Freshly Prepared)	No Expansion
6. Ammonium Nitrate +2% (NH ₄) ₂ SO ₄	36.5
7. Ammonium Nitrate +2% NH ₄ H ₂ PO ₄	36
8. Ammonium Nitrate +2% (NH ₄) ₂ HPO ₄	36
9. Ammonium Nitrate +2% K ₂ SO ₄	No Expansion
10. Ammonium Nitrate +2% Ca (NO ₃) ₂	35
11. Ammonium Nitrate +2% Ca (H ₂ PO ₄) ₂	35
12. Ammonium Nitrate +2% CsNO ₃	39
13. Ammonium Nitrate +2% CaHPO ₄	35
14. Ammonium Nitrate +2% Ca ₃ (PO ₄) ₂	35
15. Ammonium Nitrate +2% CaSO ₄	35

temperature. It appears that the significant increase in the transition temperature, noticed by Griffiths³, with magnesium and calcium nitrate is due mainly to the dehydrating influence of these salts. No transition was observed in the sample containing potassium nitrate in the temperature range studied viz. 20 to 50°C. In fact, present studies indicate that other potassium salts, viz. chloride, sulphate and dichromate of potassium, are equally effective in preventing the transition. Here too potassium nitrate formed as a result of double decomposition reaction between ammonium nitrate and the potassium salts is probably responsible for shifting the transition temperature out of the temperature range studied. Results with 2 per cent ferrous sulphate as additive were peculiar. The freshly prepared sample—reddish-brown in colour—did not show any evidence of transition. The sample, however, changed its colour to pale yellow on standing overnight. This pale yellow sample underwent transition as usual. On exposure to gaseous ammonia, the pale yellow variety reverted back to the reddish brown which again showed no transition.

Shneerson¹⁰ et al reported that the transition temperature of CAN was on the higher side as compared to the pure ammonium nitrate. This increase in the transition temperature, according to the above authors, was due either to the presence of calcium carbonate or to a small amount of calcium nitrate formed *in situ* in the product. Our results (Table 2) indicate that there is no difference between the transition temperatures of ammonium nitrate and CAN. The extent of dilution

also has no effect on the transition temperature, and CAN with 25, 20.5 and 16 per cent nitrogen underwent transition at practically the same temperature. No difference was observed when the diluent was changed. Kaolin, pure chalk and limestone diluted products gave the same transition temperature. Variation in the particle size of the limestone also does not have any effect on the temperature of transition. Potassium salts were found to be equally effective in the case of CAN (Table 2), but the addition of ferrous sulphate, did not have any effect on its transition temperature.

TABLE 2—TRANSITION TEMPERATURE OF VARIOUS SAMPLES IV→III CAN

Sample	Transition Temperature, °C IV→III
1. Ammonium Nitrate	36
2. Calcium Ammonium Nitrate (CAN) 20.5% N diluent Limestone	35-36
3. CAN (20.5% N) diluent dolomite	35-36
4. CAN (20.5% N) diluent Kaolin	36
5. CAN (25% N) diluent limestone	35-36
6. CAN (16% N) diluent limestone	35-36
7. CAN (20.5% N)+2% KNO ₃ diluent limestone	No Transition
8. CAN (20.5% N)+2% K ₂ SO ₄ diluent limestone	No Transition
9. CAN (20.5% N)+2% KCl	No Transition
10. CAN (20.5% N)+2% FeSO ₄ diluent limestone	36
11. CAN (20.5% N)—diluent limestone Hard spherical plant product	35-36
12. CAN (20.5%)+2% (NH ₄) ₂ SO ₄ * diluent limestone	37

*Ammonium sulphate added to ammonium nitrate melt at 120°C prior to the mixing of limestone.

To determine the effect of phase transition on the granules of CAN two sets of experiments were conducted. In the first series, 10 g. of spherical granules of CAN were taken in a small measuring cylinder and subjected repeatedly to the alternate cycle of heating and cooling to 50 and 20°C respectively. The expansion in volume was plotted against the number of cycles, which showed that the bulk volume increased during each upward transition IV→III (Fig. 1). The corresponding contraction during the transition III→IV appeared to be negligible and for all practical purposes it appeared as though the sample underwent irreversible expansion. The maximum swelling occurred in the granules on the top layer where they were free to expand.

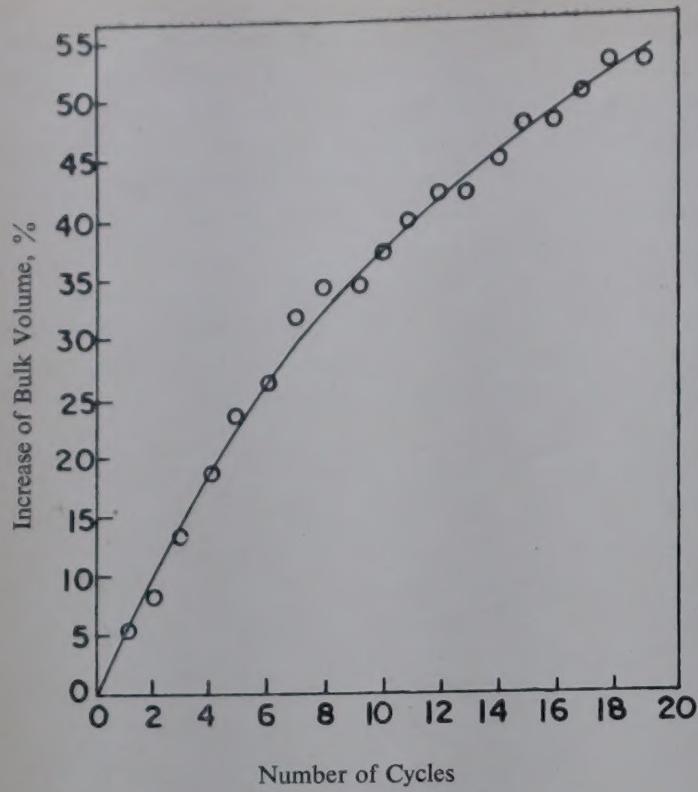
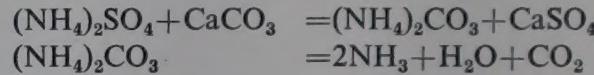


Fig. 1—Change in Bulk Volume of CAN (Spherical-Granules 3-4 mm. DIAM) on Repeated Cycling between 20 and 50°C.

In another set of experiments, a small quantity of sample (10 to 15 granules) were taken in a conical flask where the granules could expand freely and subjected to alternate cycles of heating and cooling. The individual granules were examined closely after each cycle of temperature change under a magnifying glass. After a few cycles of heating and cooling, fine cracks appeared on the surface of one granule which later spread to all the granules. The cracks multiplied and widened

as the number of cycles increased and finally the granules started disintegrating (Table 3).

The significant feature of these observations is that the granular sample of CAN undergoes irreversible expansion and the granules go on swelling till they disintegrate. Diluted ammonium nitrate is more stable and survives a greater number of cycles than pure ammonium nitrate. The stability decreases with the increase in the nitrogen content of CAN. The product containing 20.5 per cent nitrogen is more stable than CAN with 25 per cent nitrogen. The samples of CAN (25 per cent) containing 2 per cent ammonium sulphate were found to be relatively stable and survived a larger number of cycles of phase transition. Complete disintegration occurred only after 42 cycles of temperature fluctuation, whereas CAN (25 per cent) disintegrated only after 16 cycles. Addition of ammonium sulphate, during granulation, to the molten slurry of ammonium nitrate and limestone containing about 5 per cent water and at 120°C caused copious evolution of ammonia. Moist ammonium sulphate reacts with limestone even in cold releasing ammonia. The reaction occurring may be represented as follows:



The stability of CAN granules containing 2 per cent ammonium sulphate as compared to the pure CAN granule may be explained as follows. According to the accepted mechanism the cementing force between the particles constituting a granule may arise due to partial fusion, chemical reaction or by crystallization^{15,16}. In the case of CAN or ammonium nitrate, the solid bridges

TABLE 3—STABILITY OF CAN GRANULES TOWARDS REPEATED PHASE TRANSITION

Sample	Size of the Granules, mm	Appearance of Slight Cracks, No. of Cycles	Major Cracks in all Granules, No. of Cycles	Loss of Granular Shape and Start of Disintegration, No. of Cycles
1. Ammonium Nitrate*	2-4	4	7	13
2. Calcium Ammonium Nitrate (CAN) (20.5% N)	2-4	6	16	23
3. CAN (25% N)	2-4	6	9	16
4. CAN* (20.5% N)	2-4*	7	18	25
5. CAN (20.5% N) Smaller Granules	av. diam. 2.5	10	20	34
6. CAN (20.5% N) Large Granules	av. diam. 4.8	5	14	22
7. CAN* (25% N)+2% $(\text{NH}_4)_2\text{SO}_4$	2-4	13	21	42
8. CAN* (25% N)	2-4	7	10	18
9. CAN* (25% N)+2% KNO_3	2-4	No change	No change	No change

*Laboratory prepared samples.

Diluent used in all the cases was limestone.

are formed as a result of crystallization of ammonium nitrate from the melt during cooling and drying of the product. As long as these linkages are intact, the granule maintains its shape and size; these are, however, weakened and completely destroyed by repeatedly passing ammonium nitrate or CAN through the transition temperature due to the severe structural changes occurring during IV \rightarrow III transition². In the event of a chemical reaction occurring during granulation, as is the case in presence of ammonium sulphate, the reaction products themselves provide supplementary linkages. Thus, the calcium sulphate formed by the reaction of ammonium sulphate and calcium carbonate is likely to provide such links which will be immune to changes occurring during the phase transition and thus stabilize CAN.

Greater stability of smaller spherical granules of CAN towards the phase transition as compared to larger ones is significant. This is understandable because the stress to which the surface layer is subjected is due to the expansion of the whole mass of the granule. The surface layer yields to the stress because of the weakening of the linkages on account of phase transition and cracks appear. This stress will be less in the case of the smaller granules than the larger ones because of the low surface/volume ratio. Furthermore, the strain on the surface increases with the ammonium nitrate content of the

granule and the stability decreases as confirmed experimentally along the series:

CAN (20.5 per cent N) > CAN (25 per cent N) > Ammonium Nitrate.

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Design of Catalytic Naphtha Steam Reformer for Production of Synthesis Gas

By

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In this paper, the various aspects of design of naphtha steam reformer, viz. the prediction of gas and feed compositions, naphtha throughput/hour, pressure drop in the bed, reaction rate, catalyst volume requirement, tube sizing and tube life, have been dealt in details and suitable figures and tables have been provided to assist in the design calculations. A design example for generation of synthesis gas for manufacture of 100 te/day methanol has been added to elucidate the calculation procedure.

With the appearance of selective catalysts manufactured by the Imperial Chemical Industries and other firms, which has enabled much lower steam-to-carbon

ratios to be used in the steam-reforming of light distillates without carbon deposition, naphtha steam-reforming has become one of the cheapest sources of

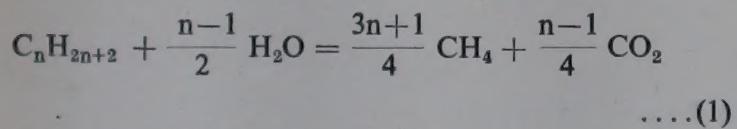
hydrogen for manufacture of ammonia, methanol, etc. A lot of work has been done in this Division of FCI Ltd on kinetic studies and catalyst development and also on pilot plant studies on naphtha steam-reforming using a catalyst developed here. Therefore, it is now appropriate to develop a simple technique for the design of a naphtha steam-reformer for synthesis gas production.

Design Procedure

The design procedure discussed here is based on a feedstock composition represented by $(CH_{1.84})_7$, for which C/H ratio is 6.53. It has been divided into three sections, the first section (I) dealing with the calculation of product gas composition at any point in the catalyst bed corresponding to a particular temperature and pressure at that point and a particular reformer feed composition. The second section (II), dealing with the catalyst volume requirements from the reaction rate point of view, provides a preliminary design of reformer tube size and numbers; it also gives the pressure drop in the catalyst bed. The third (III) deals with the tube life, permissible heat flux at any point in the tube and the length of the reformer tube required corresponding to a particular internal diameter of the tube specified by section II. In case the tube length specified by section III does not agree with that specified by section II, the preliminary design of tube size and numbers are changed and section III repeated until a reasonable check is obtained.

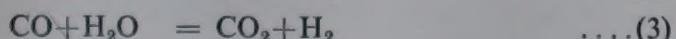
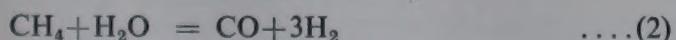
Details

Section I: Naphtha-steam mixtures undergo an initial methanation reaction which for all practical purposes may be assumed to be complete at the feed end of the reformer^{1,2}. The methanation reaction is expressed² as



where for light naphtha n is usually taken as 7.

CH_4 formed by reaction 1 then undergoes reversible reactions with steam in the following way:



The gas composition at any point would, therefore, be obtained from an approach to equilibrium of reforming and shift reactions (reactions 2 and 3 respectively). The approach depends on space velocity, mass velocity, temperature, pressure and methane content in the outlet gas. For the usual commercial reforming

conditions, the approach to equilibrium for reforming reaction may be taken as 50°F above 2 per cent methane (dry basis) in gas. Below 2 per cent methane, the approach to equilibrium should better be taken as 70°F for design purposes. For the shift reaction, the design value of equilibrium approach may be taken as 0°F.

The procedure for predicting the product gas composition with a reformer feedstock composition of $(CH_{1.84})_7$ is given below. Case (a)—Feed containing naphtha, steam and recycle hydrogen (for ammonia or methanol synthesis)

Let steam in feed/C in feed naphtha = a moles/atom

H ₂ in feed/	" "	= x " "
CH ₄ in product/	" "	= b " "
CO ₂ in product/	" "	= c " "
via shift reaction		

Then from stoichiometry, the following relations are found to hold for product gas, based on one atom of carbon in the feed naphtha.

CH ₄	= b moles	1
CO ₂	= c moles	2
CO	= 1-(b+c) moles	3
H ₂	= 1.92+x+c-3b moles	4
H ₂ O	= a+b-1-c moles	5
Total, Z	= a+1.92+x-2b moles	6

The equilibrium constants K_2 for shift and K_1 for reforming reactions have been given in Figs. 1-3. If the temperature at the point at which gas composition is desired is $\theta^{\circ}F$, then K_2 at $\theta^{\circ}F$ and K_1 at (θ —approach to equilibrium, °F) have to be determined.

$$\text{Then } K_2 = \frac{(c) \times (1.92+x+c-3b)}{[1-(b+c)] \times (a+b-1-c)} \quad \dots(4)$$

$$\text{and } K_1 = \frac{[1-(b+c)] \times (1.92+x+c-3b)}{(b) \times (a+b-1-c)} \times \left(\frac{P}{Z}\right)^2 \quad \dots(5)$$

where P = total pressure (atm) at that point.

The solutions of equations 4 and 5 may be done as follows: For particular values of a and x, first a value of b is assumed, and by trial and error the value of c which satisfies equation 4 is found out. These values are then put in equation 5. If equation 5 is not satisfied, another value of b is assumed and the process is repeated till equation 5 is satisfied.

For this calculation, the total pressure at a particular point may be estimated as inlet pressure—(inlet pressure —outlet pressure) × fraction of total reaction expected at the point. The outlet pressure may be assumed as 88-90 per cent of the inlet pressure.

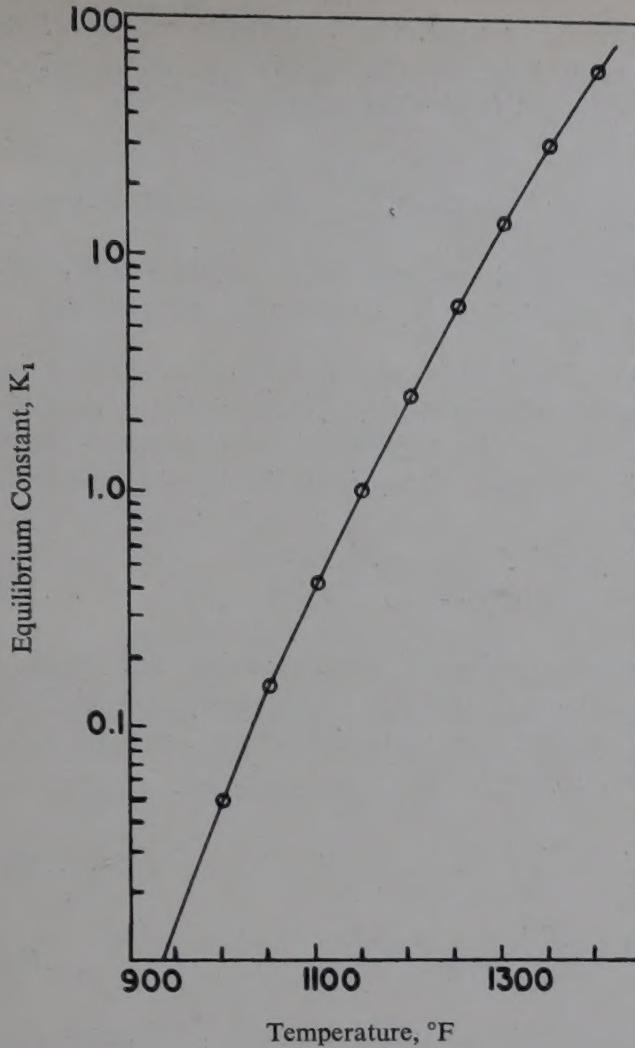


Fig. 1—Equilibrium Constant for Methane-Steam Reaction at Atmospheric Pressure

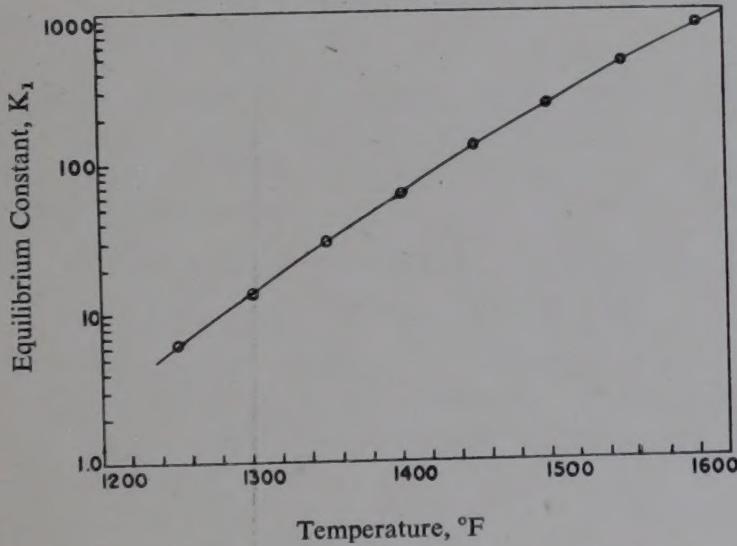


Fig. 2—Equilibrium Constant for Methane-Steam Reaction at Atmospheric Pressure

Case (b)—Feed containing naphtha, steam, recycle hydrogen and recycle carbon dioxide (for methanol and butanol synthesis). If carbon dioxide in feed/c in feed naphtha=y moles/atom, then the following sto-

chiometric relations may be written based on one atom of c in feed naphtha.

$\text{CH}_4 = b$	moles	1
$\text{CO}_2 = c+y$	"	2
$\text{CO} = 1-(b+c)$	"	3
$\text{H}_2 = 1.92+x+c-3b$	"	4
$\text{H}_2\text{O} = a+b-1-c$	"	5
$Z = a+1.92+x+y-2b$	"	6

Having these relations and the equilibrium constant values K_1 and K_2 , the product gas composition at any point of the bed may be calculated as before.

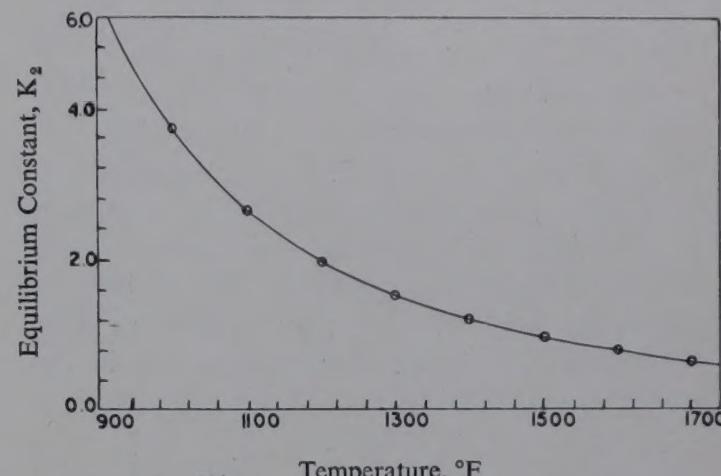


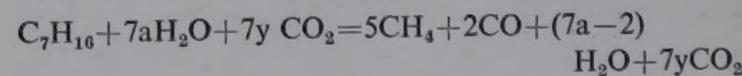
Fig. 3—Equilibrium Constant for Shift Reaction at Atmospheric Pressure

Section II: The rate of reaction of naphtha with steam has been given by Ghosal¹ et al as:

$$r = 5.0 \times 10^{-2} \left(\frac{\text{C}_{\text{H}_2}}{\text{C}_{\text{H}_2\text{O}}} \right)^{0.662} \frac{G^{0.59} T^{0.14} (P_{\text{CH}_4} - P_{\text{CH}_4})}{\mu^{0.10} d p^{1.41} M_m (P + 2P_{\text{CH}_4})} \text{ l.m. eq} \quad \dots (6)$$

where r is given in terms of lb moles of CO and CO_2 produced via reforming and shift reactions per hour/cft catalyst in the heated zone. In the evaluation of

($P_{\text{CH}_4} - P_{\text{CH}_4}$) l.m. and ($P + 2P_{\text{CH}_4}$) l.m., the partial pressure of methane at the inlet to the catalyst bed has been based on the following methanation reaction:



So that partial pressure of methane at the inlet,

$$P_{\text{CH}_4 i} = \frac{5}{5+7a+7y} P_i \quad \dots (7)$$

This rate equation has been developed on laboratory kinetic data with ICI 22-1 catalyst containing 15 per cent Ni in a 1" tube under atmospheric pressure. From pilot plant tests under higher pressures with FCI CD-RN-

33 naphtha steam-reforming catalyst in a $2\frac{1}{2}$ " i.d. $\times 3$ " o.d. tube of heated length 10', it has been found that the rate is about 1.40 times higher than predicted by equation 6. For design purposes, a rate 1.20 times higher than provided by equation 6 may be taken.

From an analysis of equation 6, it is found that the rate depends on five factors, viz. (a) catalyst particle size, d_p , (b) gas mass velocity, G , (c) outlet temperature, T , (d) feed composition and (e) outlet composition; the last three of the above are specified by section I.

CHOICE OF CATALYST SIZE—This Division has started producing naphtha reforming catalyst of many different sizes, like (a) $5/8$ " o.d. $\times 1/4$ " i.d. $\times 3/8$ " long rings, (b) $9/16$ " i.d. $\times 1/4$ " o.d. $\times 3/8$ " long rings and (c) $3/8$ " dia $\times 3/4$ " long cylinders, etc. This design procedure has been dealt with the above three sizes of the catalyst.

CHOICE OF MASS VELOCITY—For the preliminary design of catalyst volume requirements, mass velocity, G , may be so chosen as to give a pressure drop of about 10-12 per cent of inlet pressure in the catalyst bed the average packed height of which may be taken as close to 25 feet as a first choice. The pressure drop in the catalyst bed is calculated by the following equation³:

$$\frac{\Delta P'}{L_f} = \frac{G}{144 \cdot g \cdot D_p} \frac{(1-\epsilon)}{\epsilon^3} \left[\frac{150(1-\epsilon)\mu}{D_p} + 1.75 G \right] \quad \dots(8)$$

In this equation D_p , the characteristic diameter has been taken as equal to $\frac{6}{S/V}$. For calculation of pressure drop in a long bed, log mean, average properties of

ρ and μ should be used. The void fraction, ϵ is a function of catalyst particle dia to tube i.d. and this value may be obtained from Calderbank etc.⁴

For ease of calculations, $\frac{\Delta P'}{L_f}$ has been shown against

G for three usually encountered inlet and outlet conditions for several sizes of catalysts (Fig. 4, Table 1).

Since b is the fraction of C in feed naphtha remaining unconverted in the form of CH_4 in the outlet gas and the mol. wt. of naphtha represented as $(CH_{1.84})_7$, is 96.88, the design naphtha throughout in kg./hr. (catalyst) would be

$$\frac{r}{1-b} \times 0.221 \quad \dots(9)$$

Preliminary Design of Tube Dimensions and Numbers

If V is the total volume of catalyst required for a specified amount of naphtha fed per hour and W =total mass flow, lbs/hour, then

$$V = \frac{\pi D_i^2}{4} N \cdot L \quad \dots(10)$$

$$\text{and } W = \frac{\pi D_i^2}{4} N \cdot G \quad \dots(11)$$

From equation 11 assuming a value of N , number of tubes, the value of the tube i.d. D_i from known values of G and W is obtained. Putting these values of N and D_i in equation 10 the heated length L , is obtained.

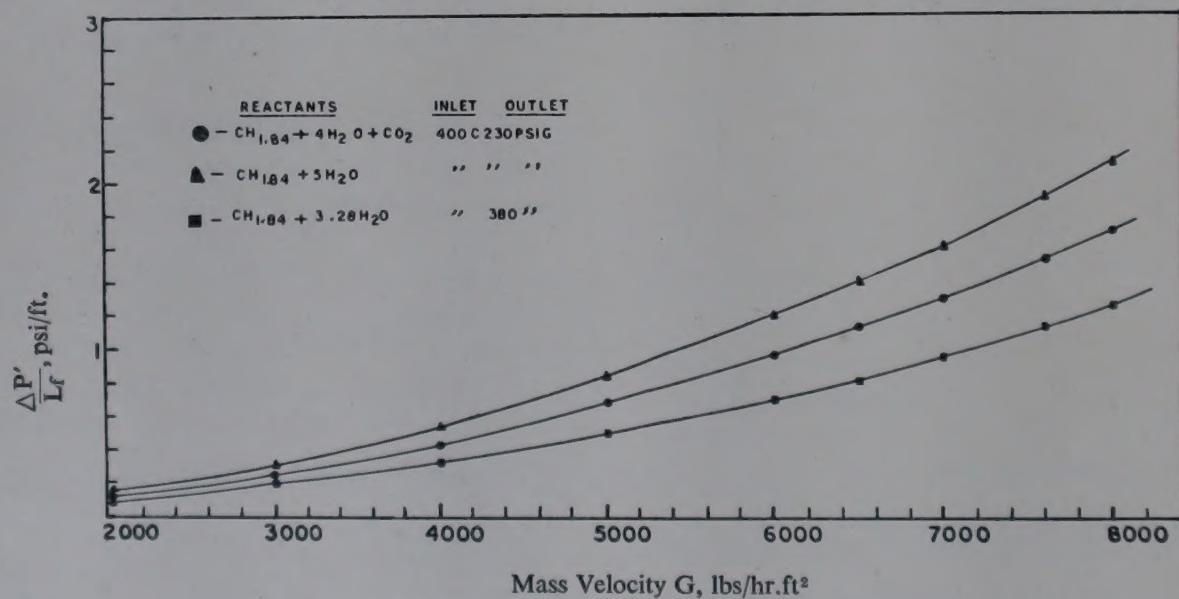


Fig. 4—Pressure Drop in $4\frac{1}{2}$ " id tube with $5/8" \times 1/4" \times 3/8"$ long rings. For other pressures $\Delta P'/L_f \propto \frac{1}{\text{Pressure}}$. For other sizes of tubes and catalyst refer to Table 1.

TABLE 1—RELATIVE PRESSURE DROP & HEAT TRANSFER COEFFICIENTS FOR DIFFERENT TUBE AND CATALYST SIZES

Item	Tube Size	Catalyst Size	Pressure Drop Index	Heat Transfer Coefficient Index
1.	4 $\frac{1}{2}$ " i.d.	5/8" x 1/4" x 3/8" L rings	100 (Pr. drop for this has been shown in Fig. 4)	101.3
2.	-do-	9/16" x 1/4" x 3/8" L rings	113.5	106.5
3.	-do-	3/8"D x 3/4"L cylinders	85.0	114.5
4.	3 $\frac{3}{8}$ " i.d.	5/8" x 1/4" x 3/8" L rings	95.0	100 (heat transfer coefficient for this has been shown in Fig. 7)
5.	-do-	9/16" x 1/4" x 3/8" L rings	108.5	105.0
6.	-do-	3/8"D x 3/4"L cylinders	82.5	113.2
7.	-do-	1/4"D x 1/4"L cylinders	170.0	188.5

Section III—Final Design of Tube Size, Thickness and Numbers: Tube length obtained in section II is limited by permissible heat flux through the tube wall material for a specified tube life. The maximum allowable heat flux and hence the temperature gradient across the wall at any point is limited by permissible total stress due to pressure and temperature gradient for a specified tube design life. The pressure stress, S_p , for a thin-walled cylinder is given as $S_p = \frac{PD_1}{D_o - D_1} \dots (12)$

The thermal stress S_t , for a thin-walled cylinder has been given by Raymond⁵ et al as $S_t = \frac{1}{2} \Delta t \alpha E / (1 - m) \dots (13)$

At the present moment, the most widely used tube material is centrifugally cast HK 25/20 Cr-Ni alloy (ASTM A-362), the properties of which for the purpose of this design are as follows:

$$\alpha = 17.946 \times 10^{-6} / ^\circ\text{C} \text{ and } m = 0.28$$

E is a function of temperature. Its values, taken from Clark⁶ and Dieter⁷, have been plotted against temperature (Fig. 5). For ease of calculation the value of $S_t / ^\circ\text{C}$ have also been given.

The allowable total stresses for the three different

design lives have been drawn based on data given by Edeleanu⁸ (Fig. 6).

WALL THICKNESS—A negligible heat flux at the outlet end of the reformer tube is assumed and the maximum design wall temperature at that point is taken as 100–120°C higher than the outlet gas temperature. The thermal stress here being negligible, the total allowable stress is equated to pressure stress to find D_o and hence the wall thickness (equation 12). To this about 1/16" extra is provided for machined tube and about 1/8" extra is provided for sandblasted tube.

Calculation of Tube Length Required for the Desired Degree of Reaction—For this a stagewise calculation is done. The total temperature rise of a gas in the reformer tube is divided into several steps. Thus, for a 400°C inlet temperature the steps may be 100°C per step upto 700°C, 50°C per step upto 800°C and 25°C per step upto 875°C. The gas composition at the end of each step and the flow/tube/hour are calculated as per sections I and II. Then from the heats of reactions 1, 2 and 3 (Table 2) and the specific heats of gas components, the heat load Btu/(hr) (tube) for each step may be calculated. The heats of the above three reactions (Table 2) have been given by Lihou².

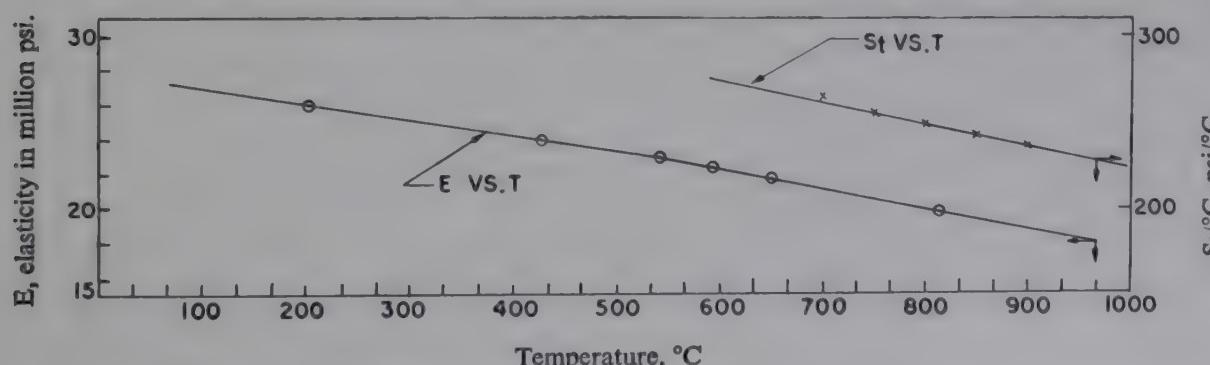


Fig. 5—Elasticity and Temperature Stress for 25/20 H.K. alloy

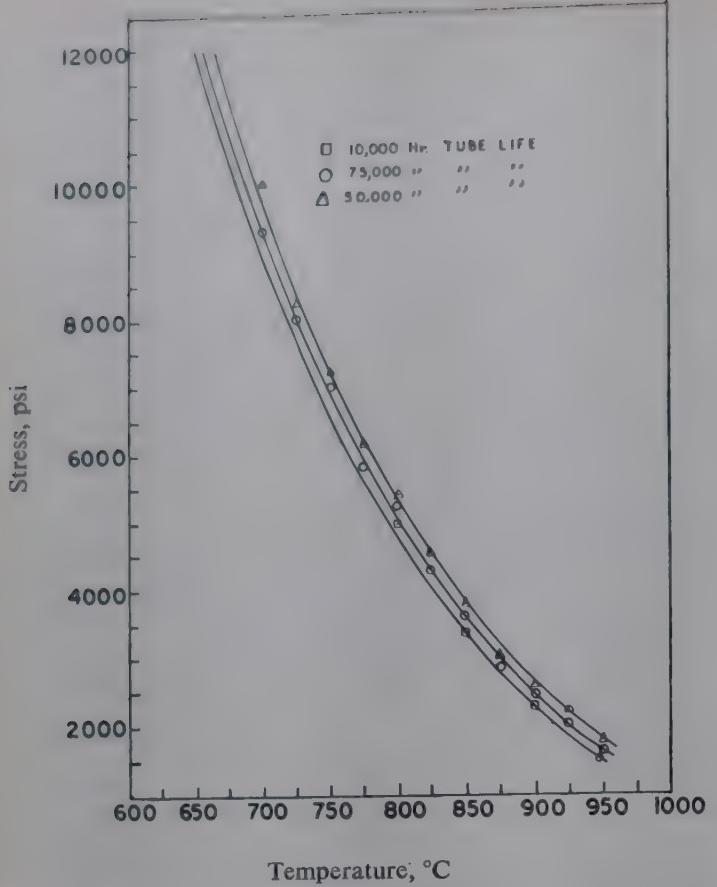


Fig. 6—Stress Curve for 25/20 H.K. Alloy (A.S.T.M.—A—362, 25/20 Cr/Ni) Centrifugally Cast Tube

TABLE 2—HEAT OF REACTIONS, Cal/g. mol.
(DATA AT ATMOSPHERIC PRESSURE)

Temperature, °C	Heat of Reactions for		
	Reaction 1	Reaction 2	Reaction 3
400	—	52.5×10^3	-9.15×10^3
450	-24.2×10^3	—	—
500	—	53.1×10^3	-8.90×10^3
600	—	53.45×10^3	-8.62×10^3
700	—	53.70×10^3	-8.40×10^3
800	—	54.05×10^3	-8.20×10^3
900	—	54.20×10^3	-7.98×10^3

The heat transfer surface and consequently the heated length required for each step may be calculated from the following heat transfer relations:

$$q = h \pi D_i L (t_o - t_i) \times 1.8 \quad \dots(14)$$

$$= K_w \pi D_o L \frac{(t_o - t_i) \times 2 \times 1.8}{(D_o - D_i) \times 12} \quad \dots(15)$$

$$= 0.173 F \pi D_o L [(T_g/100)^4 - (T_o/100)^4] \quad \dots(16)$$

Heat Transfer Coefficient, h —The value of h may be obtained from an equation⁴, which is as follows:

$$\frac{h d_p}{Kg} = 3.6 \left(\frac{d_p G}{\mu} \right)^{0.365} \quad \dots(17)$$

For each step, values of μ and K_g should be taken at the average temperature. The calculated values of h for different catalyst sizes and tube sizes have been shown in Fig. 7 and Table 1.

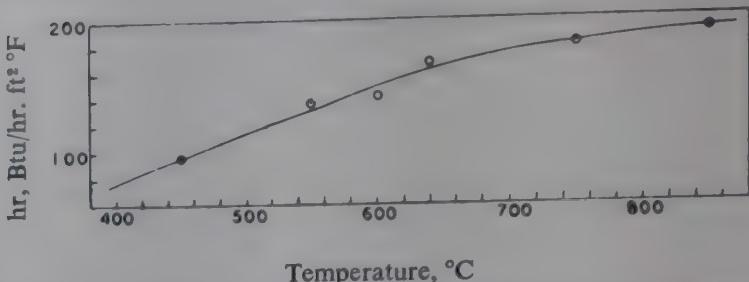


Fig. 7—Heat Transfer Coefficient for 5/8" x 1/4" x 3/8" Long Rings in 3 1/2" id Tube for $G = 6000$ lbs/h. ft. (For other values of G , $h \propto G^{0.365}$.)

Wall Conduction Coefficient, K_w —The wall conduction co-efficient for HK. 25/20, Cr/Ni may be taken as 200 Btu/(hr) (ft²) (°F/in) at the working temperature of a steam reformer².

Radiation Exchange Factor, F —This exchange factor may be taken² as 0.5.

Conductivity & Viscosity of Gas-Steam Mixtures.—For normal steam-gas mixtures the conductivity and viscosity at different temperatures may be taken as given in Table 3.

TABLE 3—VISCOSITY AND CONDUCTIVITY OF STEAM-GAS MIXTURES NORMALLY ENCOUNTERED IN STEAM REFORMING
(Average Values)

Temperature of Gas, °F	Viscosity, lbs/ft/ (hr)	K_g Btu/(hr) (ft ²) (°F/ft)
1100	0.075	0.076
1200	0.080	0.083
1300	0.085	0.093
1400	0.092	0.102
1500	0.097	0.110
1600	0.102	0.120
1700	0.107	0.130

The solutions of equations 14, 15 and 16 may be done in the following way: An average value of mean wall temperature is estimated in each step and the corresponding allowable total stress for a specified tube life is obtained from Fig. 6. The pressure stress is subtracted from the total stress to give allowable thermal stress. Then $\Delta t = t_o - t_i$ corresponding to the allowable thermal stress is obtained from Fig. 5. This value of Δt is substituted in equation 15 to get the heated length required for any step. Substituting the value of L in equation 14 we will get t_i and therefore t_o . The mean of t_o and t_i gives the average value of mean-wall tem-

perature in a particular step. If this calculated average mean-wall temperature does not agree with the estimated value, another value is estimated and the same calculations repeated till checked. The flue gas temperature is then calculated from equation 16. The total heated length of the reformer is now obtained by summing up lengths required for individual steps and this is then checked with the length obtained in Section II.

If they do not agree the preliminary design of reformer tube size and numbers are changed and section III repeated till these agree.

Design Example

About 14500 Nm³/h of synthesis gas of the following composition is desired for manufacture of 100 te/day of methanol. The desired outlet pressure is 14 kg/cm²g, for which a suitable reformer is to be designed. The composition of gas (per cent by wt.) is as follows: CO—22.32; CO₂—27.23; H₂—49.54; and CH₄—0.91.

Solutions

(a) *Inlet Pressure*—Assuming 11 per cent pressure drop in the bed, the inlet pressure would be 15.5 kg/cm²g.

(b) *Feed Composition*—The feed composition is so assumed that a=4, y=1 and x=0.07.

(c) *Outlet Gas Temperature*—From the method given in section I, the outlet equilibrium temperature corresponding to above feed composition would be 825°C and the actual outlet gas temperature 865°C for the desired outlet gas composition.

(d) *Catalyst Size*—The catalyst size is chosen as 5/8" o.d. × 1/4" i.d. × 3/8" L rings.

(e) *Allowable Mass Velocity, G*—For a pressure drop of about 22 psi in a packed length of about 23.6 feet, the allowable mass velocity G is read from Fig. 4 as 5930 lbs/(h) (ft²).

(f) *Catalyst Volume Required for the Desired Reaction*

—From material balance naphtha throughput required for generating 14,500 Nm³/h gas comes to 2260 kg/h and the total feed mixture throughput to 46700 lbs/h.

Now since d_p=0.0595 ft, C_{H₂}/C_{H₂O}=0.665

G=5930 lbs/(h) (ft²), T=1138°K, μ=0.102 lbs/(ft) (h), M_m=18.7. Hence from equation 6, r=1.83 lb moles/(hr) (ft³ cat) p_{CH_{4,i}}=2.063 atm, p_{CH_{4,o}}=0.078 atm, p_{CH_{4,eq}}=0.039 atm. Design value of r=1.2×1.83=2.2 lb moles/(h) (ft³ cat). Hence from equation (9)

design naphtha throughput in Kg/(h) (l. cat.) = $\frac{2.2}{1-b} \times$

$$0.221 = \frac{2.2}{1-0.036} \times 0.221 = 0.503.$$

Therefore catalyst volume required=4500 l.=158 cft.

(g) *Preliminary Design of Tube Size and Numbers*—Since G=5930 lbs/(hr) (ft²), w=46,700 lbs/hr. hence from equation 11, assuming N=110 tubes, D_f=0.302 ft=3⁵/₈ inches. Putting these values in equation 10, L=20 feet heated length. Hence, the packed length may be 23 feet and total length 25 feet.

(h) *Tube Wall Thickness*—Assuming design tube life of 100,000 hours and maximum design wall temperature at the outlet as outlet gas temperature +110°C that is 975°C, the permissible total stress is 1150 psi. Hence, from equation 12 wall thickness comes as 0.347 inches. Adding 1/16" extra for machined tube and rounding up a 7/16" wall thickness is selected.

(i) *Final Design of Tube Size Based on Allowable Heat Flux for a Particular Tube Life*—For this calculation, the total temperature rise in the catalyst bed was divided into five steps of 110°, 111°, 111°, 61° and 71°C from feed end to outlet end and the gas compositions at the exit of each step were calculated as under section I. Knowing the naphtha flow as well as total mass flow/tube/hour, the heat load in Btu/(hr) (tube) may also be calculated (Table 4).

TABLE 4—STEPWISE CALCULATION OF GAS COMPOSITION* AND HEAT LOAD/(tube) (h)

Step	Pressure, ata	Outlet temp., °C	Gas Composition of Feed Naphtha, moles/atom						lbs/(hr.) (tube)	Btu/(hr) (tube)
			CO	H ₂	CH ₄	CO ₂	H ₂ O	Total		
1.	16.5	511	0.045	0.465	0.62	1.335	3.285	5.75	46	52. 3 × 10 ³
2.	16.5	622	0.15	0.80	0.51	1.34	3.17	5.97	—	75.56 × 10 ³
3.	16.0	733	0.48	1.51	0.25	1.27	2.98	4.49	—	123.54 × 10 ³
4.	15.5	794	0.71	1.84	0.11	1.18	2.93	6.77	—	71.25 × 10 ³
5.	15.0	865	0.884	1.962	0.036	1.08	2.956	6.92	—	50.46 × 10 ³

*Gas composition after methanation reaction per atom C in feed naphtha

CH₄=0.7857 Moles CO₂=0.2143, Moles.

H₂O=a=0.4286=3.5714 Moles

Then from solutions of equations 14, 15 and 16 following the procedure in section III the heated length necessary for each step may be found out. The results of these calculations for design tube life of 100,000 and 75,000 hours are given below (Tables 5 and 6).

Thus, a 21.7 feet heated length for 75,000 hours tube-life confirms more or less the preliminary design. The number of tubes required for this length would be $110 \times 20 / 21.7 = 103$. So 104 tubes $3\frac{1}{8}$ " i.d. $\times 4\frac{1}{2}$ " o.d. having 21.70 feet heated length may be selected for the final design of the reformer. Now G will be 6270 lbs/(h) (ft^2) for which increase in pressure drop per ft will be slightly higher, but the total pressure in a packed length of 24 ft will be about 25.0 psi which is very close to the assumed figure of 22 psi. The packed length may be assumed 24.0 feet and the total length taken as 27 feet.

Furnace Sizing and Tube Layout: Furnace efficiency for a steam-reformer may be assumed as 50 per cent, so that the total heat release required is twice the total

heat absorption. Such types of furnaces are usually designed on the basis of a space rate of heat release of about 10,000 to 12,000 Btu/(h)/(ft^3 furnace volume). The furnace may be fired with horizontally placed flat-flame type burners the capacities of which are varied at different levels in proportion to heat absorption rate per foot of tube in different zones (Tables 5 and 6). For horizontally fired furnaces the tubes may be laid out in two rows with a pitch/diameter ratio of about 2.5 along and between the rows. The rows of tubes should be kept about $3\frac{1}{2}$ feet away from the burner mouths to prevent flame impingement. The burners may be placed at 4 different levels $1\frac{1}{2}$ feet, $4\frac{1}{2}$ feet, 9 feet and 15 feet from the feed end respectively with capacities in the ratio of 4 : 3 : 2 : 1 respectively.

It has become more or less a standard practice to select a pitch/diameter ratio of about 2-3 in reforming furnace design. Higher pitch/diameter ratio would give a better radiative heat transfer and more uniform skin temperature but then furnace size will be larger and *vice versa*.

TABLE 5—CALCULATION OF HEATED LENGTH FOR TUBE DESIGN LIFE OF 100,000 HOURS

Step	Gas Temp., °C		Average Wall Temp., °C		Average Heat Flow, Btu/(hr)	Average Flue Gas Temp., °C	Heated Length, ft
	Inlet	Outlet	Inner	Outer	(ft)		
1.	400	511	604	649.7	40,000	1225	1.31
2.	511	622	664.5	698.1	29,400	1140	2.61
3.	622	733	739.1	761.1	19,300	1070	6.40
4.	733	794	801.0	815	12,500	1015	5.70
5.	794	865	853.7	862.5	7,750	987	7.02

Total length=23.04 ft.

TABLE 6—CALCULATION OF HEATED LENGTH FOR TUBE DESIGN LIFE OF 75,000 HOURS

Step	Gas Temp., °C		Average Wall Temp., °C		Average Heat Flow Btu/(hr.)	Average Flue Gas Temp., °C	Heated Length, ft.
	Inlet	Outlet	Inner	Outer	(ft)		
1.	400	511	609.0	656.0	41,500	1250	1.26
2.	511	622	668.5	703.0	30,700	1165	2.49
3.	622	733	741.7	764.9	20,300	1065	6.07
4.	733	794	803.2	818.2	13,150	1025	5.42
5.	794	865	857.2	866.8	8,450	1000	6.45

Total length=21.69 feet.

Nomenclature

C_{H_2}	= Concentration of H_2 in outlet gas, lb moles/ft ³	S_t	= Thermal stress, psi.
C_{H_2O}	= Concentration of H_2O in outlet gas, lb moles/ft ³	E	= Modulus of elasticity, psi
d_p	= Surface equivalent spherical diameter, ft.	α	= Coefficient of expansion per °C
D_p	= Characteristic diameter, ft	Δt	= Wall temperature difference, °C
G	= Gas mass velocity, lbs/(hr) (ft ²)	m	= Poisson's ratio
M_m	= Mean mol. wt. of steam-gas mixture at outlet	q	= Heat load in any step, Btu/(hr) (tube)
r	= Rate of reaction, lb moles/(hr) (ft ³)	h	= Heat transfer coefficient, Btu/(hr) (ft ²) (°F)
S	= Surface of a particle, ft ²	K_w	= Thermal conductivity, Btu/(hr) (ft ²) (°F/in)
V	= Volume of a particle, ft ³	t_i	= Inner wall temp., °C
T	= Temp. of outlet gas °K	t_o	= Outer wall temp., °C
p	= partial pressure, atm.	t	= Gas temp., °C
P	= Total pressure, atm.	F	= Overall exchange factor for radiation from flue gas to tube wall
μ	= Viscosity, lbs/(ft) (h)	T_g	= Average flue gas temp in any step, °R
ρ	= Density of gas-steam mixture, lbs/ft ³	T_o	= Average outer wall temp. in any step, °R
$l.m$	= log mean	K_g	= Conductivity, Btu/(h) (ft ²) (°F/ft)
$eq.$	= Equilibrium	K_1	= Equilibrium constant for reforming reaction
P_{CH_4i}	= Inlet partial pressure of CH_4 atm.	K_2	= Equilibrium constant for shift reaction
P_1	= Total inlet pressure, atm	θ	= Temperature, °F
ΔP^1	= pressure drop, psi	Z	= Total number of moles
L_f	= packed length, feet		
g	= Acceleration due to gravity, 4.18×10^8 ft/hr ²		
ϵ	= void fraction		
L	= Heated length, ft.		
V	= Total volume of catalyst, ft ³		
D_i	= Tube i.d., ft.		
D_o	= Tube o.d., ft.		
N	= Number of tubes		
W	= Total mass flow, lbs/h		
S_p	= Pressure stress, psi		
P'	= Total pressure, psi		

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Estimation of Ammonium Salts in Fertilizers by Conductometric Titrations

By

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Conductometric titrations have been carried out with dilute aqueous alcoholic solutions (containing 20 per cent alcohol by volume) of ammonium sulphate, ammonium nitrate, mono-ammonium phosphate and diammonium phosphate against standard sodium hydroxide, taken individually, two and three at a time respectively. Results show that quick and reasonably accurate estimation of these ammonium salts in commercial fertilizers like ammonium sulphate nitrate, phosphonitric nitrophosphate and nitrophosphate (by sulphate recycle process) is possible.

Introduction

Conductometric titration is a powerful analytical tool and has a scope for wider applications in industry. There are a few references in the literature to the application of this technique in the analysis of ammonium salts and fertilizer materials. Gender¹ et al have titrated ammonium compounds conductometrically with sodium hydroxide in an aqueous medium but have not done detailed analysis of mixtures and there was also an appreciable error in their experiment. Leithe² used conductometric and potentiometric methods for the determination of ammonium salts in 50 per cent alcoholic medium by titration against sodium hydroxide. He had analysed ammonium nitrate and ammonium chloride accurately by these methods but could not estimate less soluble salts such as ammonium sulphate and mono-ammonium phosphate accurately. Some more work³⁻⁵ has been carried out on this line in recent years but detailed studies have not been made.

In this laboratory, a conductometric method for the estimation of ammoniacal and nitrate nitrogen in ammonium sulphate nitrate fertilizer⁶ has been developed. It was thought desirable to extend this work to other ammonium salts commonly met with in fertilizer materials. The compounds studied were ammonium nitrate, ammonium sulphate, mono-ammonium phosphate and diammonium phosphate. Experiments were carried out with these ingredients individually as also in various combinations. Conductometric titrations

were also carried out with samples of commercial fertilizers containing ammonium salts, such as phosphonitric nitrophosphate⁷, nitrophosphate by the sulphate recycle process⁸ and ammonium sulphate nitrate⁶ and the results of experiments are reported in this paper.

Experimental

Procedure: All the conductometric titrations were carried out with an Hungarian make conductivity meter*. A bell type electrode with three platinum rings was used in these experiments. The cell assembly with a hand-driven glass stirrer is kept in a small thermostatic water bath maintained at a constant temperature of $30 \pm 0.1^\circ\text{C}$. Above the cell assembly is fixed a microburette of 10 ml. capacity, with a least count of 0.02 ml., and the titrant is added in 0.1 to 0.5 ml. portions. All the chemicals used in these investigations were of A. R. (B.D.H.) grade and the absolute alcohol used for making non-aqueous medium for titration was supplied by M/s. Bengal Chemical & Pharmaceutical Works, Calcutta. All the solutions were made in demineralized and carbon dioxide-free conductivity water. (Conductivity: $0.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$)

The general procedure followed was to prepare appropriate sample solution in the absolute ethyl alcohol-water medium, and to titrate it with standard sodium hydroxide (0.1—0.05 N), by addition of reagent

* Radelkisz, Type OK 102

in steps until an appreciable excess was introduced. The conductance readings taken after each addition of titrant were plotted against volume of reagent added, and the end points were ascertained from the plots. The volume of the solution should not change appreciably during the titration; this was achieved by taking dilute solutions for the titration and the titrant was more than 20 times stronger than the solution to be titrated. Also a correction for the dilution effect was made in each reading by multiplying the values of the specific conductance obtained in each case by the factor $(V+v)/V$, in which V is the original volume of the solution and v is the volume of reagent added.

The concentrations of solutions of different salts and sodium hydroxide and also the proportions of alcohol and water in the media required to give sharp breaks in the titration curves leading to accurate estimations were found out by trial and error. In general, it was found that the presence of 10 to 20 per cent by volume of alcohol in the solution to be titrated was necessary for a good titration curve. The concentration of sodium hydroxide varied between 0.1 to 0.05 N. Stock solutions of dried salts of known weight (0.5 to 1 g.) were prepared in different 250 ml flasks. From these stock solutions different amounts of solutions (5 or 10 ml.) were taken for the final titration after dilution to 100 ml. or 200 ml. with requisite amount of absolute alcohol.

Systems Studied: The following four systems were studied.

(a) All the ingredients taken separately—(i) ammonium nitrate, (ii) ammonium sulphate, (iii) monoammonium phosphate and (iv) diammonium phosphate.

(b) Two of the ingredients taken at a time—(i) ammonium sulphate+ammonium nitrate, (ii) ammonium nitrate+diammonium phosphate, (iii) ammonium nitrate+monoammonium phosphate, (iv) ammonium sulphate+monoammonium phosphate, (v) ammonium sulphate+diammonium phosphate and (vi) monoammonium phosphate+diammonium phosphate.

(c) Three of the ingredients taken at a time—(i) ammonium nitrate+monoammonium phosphate+diammonium phosphate, (ii) ammonium nitrate+ammonium sulphate+diammonium phosphate, (iii) ammonium nitrate+ammonium sulphate+monoammonium phosphate, and (iv) monoammonium phosphate+diammonium phosphate+ammonium sulphate.

(d) Commercial Fertilizers—(i) double salt (ammonium sulphate nitrate) containing ammonium sulphate and ammonium nitrate, (ii) phosphonitic nitrophosphate (without diammonium phosphate) containing monoammonium phosphate and ammonium nitrate, (iii) phosphonitic nitrophosphate with diammonium phosphate and (iv) nitrophosphate (obtained by sulphate recycle process) containing monoammonium phosphate, diammonium phosphate and ammonium nitrate.

Results and Discussion

The results of conductometric titration in very dilute solutions of individual ammonium compounds with 0.05 N sodium hydroxide in a 20 per cent alcoholic medium are given in Table 1. In all cases sharp end points were obtained. Except in the case of monoammonium phosphate, the conductivity either decreases or remains constant before the end points are reached. In case of monoammonium phosphate conductivity increased first

TABLE 1—CONDUCTOMETRIC TITRATION OF SOME AMMONIUM SALTS TAKEN ONE AT A TIME AGAINST STANDARD CAUSTIC SODA (TOTAL DILUTION 100 ml.)

Stock Solutions:		Ammonium Nitrate		Ammonium Sulphate		Monoammonium Phosphate		Di-ammonium Phosphate	
No. of Observations	Vol. of Stock Soln. for Titration, ml.	A. 0.779, g./250 ml.	B. 1.470, -do-	0.500, g./250 ml.	1.001, -do-	0.502, g./250 ml.	1.001, -do-	0.502, g./250 ml.	1.005, -do-
1	5.0	15.30	15.15	0.92	9.90	9.92	0.20	9.85	9.90
A								0.50	9.80
2	7.5	23.00	22.80	0.85	14.85	15.00	1.02	14.77	14.90
3	5.0	28.40	27.80	2.10	19.80	20.12	2.10	19.60	19.82
B								1.10	19.60
4	7.5	42.60	41.60	2.11	29.95	30.65	2.28	29.40	30.01
								2.02	29.40
								29.26	0.45

due to its conversion to diammonium phosphate and then the neutralization of diammonium phosphate proceeds in the usual way. In case of concentrated ammonium sulphate solution in a 20 per cent alcoholic medium only one break is obtained but a dilute solution gives two breaks, one of which corresponds to double the quantity of alkali required for the other; this shows that the neutralization takes place in two stages. The error in all cases is within 2.5 per cent but in case of very dilute solutions the error is reduced to less than 1.5 per cent.

When mixtures of ammonium salts are titrated each component gives a sharp break, if dilute aqueous alcoholic solutions are used. The conductance of ammonium compounds as calculated from limiting ionic mobilities are in the order of monoammonium phosphate, diammonium phosphate, ammonium sulphate and ammonium nitrate. Hence if alkali is added to the mixture of these ingredients first monoammonium phosphate will be reacted and then the others will follow the order

given above. The titration curves actually obtained for a mixture of two or three ammonium compounds is found to follow the same order.

The titration curves of ammonium compounds taken two at a time are shown in Fig. 1. Curve I (Fig. 1) shows the titration of monoammonium phosphate and diammonium phosphate. The first break shows the conversion of monoammonium phosphate to diammonium phosphate and the second break corresponds to the complete neutralization of diammonium phosphate present in the system which includes the quantity initially present and that formed from monoammonium phosphate. In case of mixture of diammonium phosphate and ammonium sulphate (curve II, Fig. 1) the first break corresponds to the neutralization of diammonium phosphate and the second and third ones are due to ammonium sulphate. When ammonium sulphate and ammonium nitrate are titrated in dilute solutions (curve III, Fig. 1) the first two breaks are due to ammonium sulphate and the third one is due to ammonium

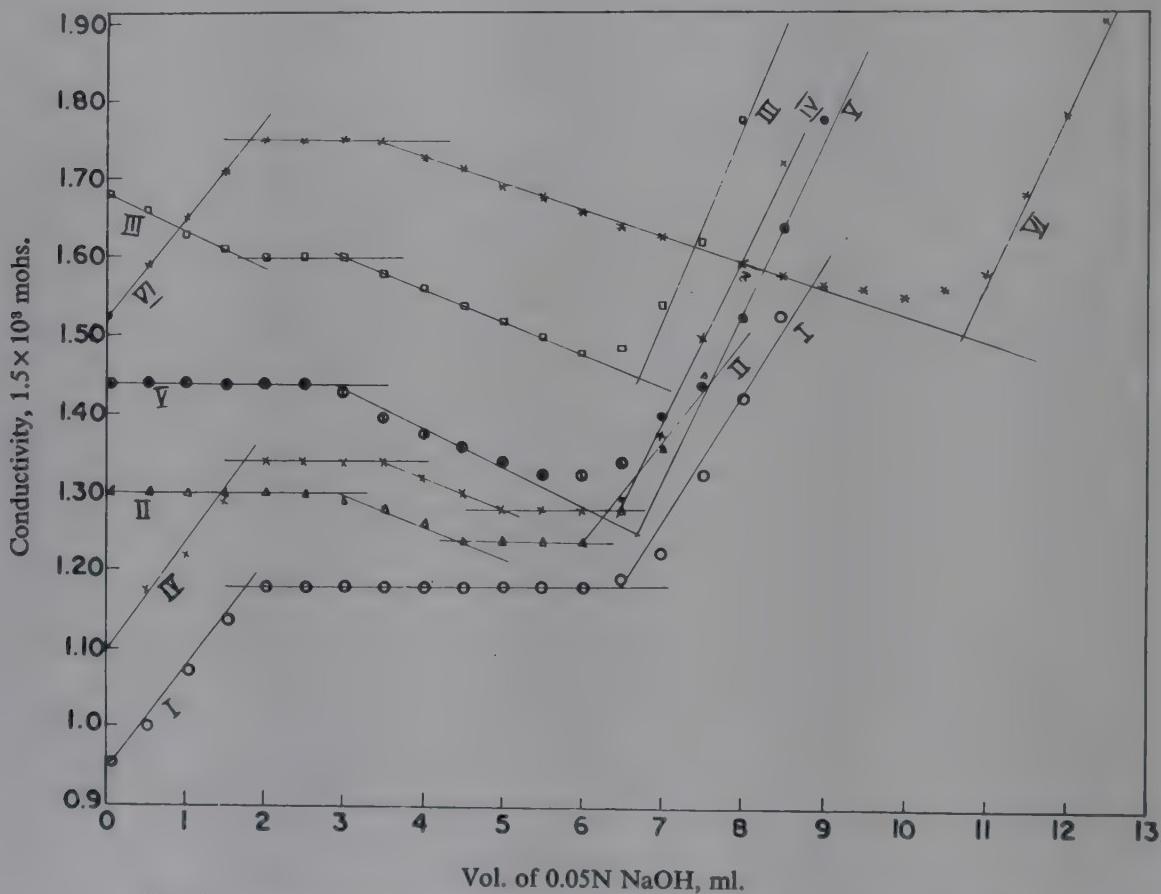


Fig. 1—Conductometric Titration of Ammonium Salts Taken Two at a Time

- I—5 ml. $\text{NH}_4\text{H}_2\text{PO}_4$ +5 ml. $(\text{NH}_4)_2\text{HPO}_4$ Stock Soln. against 0.05N NaOH
- II—5 ml. $(\text{NH}_4)_2\text{HPO}_4$ +5 ml. $(\text{NH}_4)_2\text{SO}_4$ Stock Soln. against 0.05N NaOH
- III—5 ml. $(\text{NH}_4)_2\text{SO}_4$ +5 ml. NH_4NO_3 Stock Soln. against 0.05N NaOH
- IV—5 ml. $\text{NH}_4\text{H}_2\text{PO}_4$ +5 ml. $(\text{NH}_4)_2\text{SO}_4$ Stock Soln. against 0.05N NaOH
- V—5 ml. $(\text{NH}_4)_2\text{HPO}_4$ +5 ml. NH_4NO_3 Stock Soln. against 0.05N NaOH
- VI—5 ml. $\text{NH}_4\text{H}_2\text{PO}_4$ +10 ml. NH_4NO_3

nitrate; in this particular case if we gradually increase the solution concentration a stage is reached when only two breaks are obtained—one due to ammonium sulphate and other due to ammonium nitrate. On further increasing the concentration of the solution only one break—that of complete neutralization of the two salts taken together—is obtained. The conductometric titration of a mixture of monoammonium phosphate and ammonium sulphate is given in curve IV (Fig. 1). This curve has four breaks. The first two are due to monoammonium phosphate and last two due to ammonium sulphate: here also, at a particular higher solution concentration of the mixture the last two breaks of ammonium sulphate are converted to one break at the complete neutralization of ammonium sulphate. Curves V and VI (Fig. 1) relate to mixtures of diammonium phosphate and ammonium nitrate and monoammonium phosphate and ammonium nitrate respectively. These curves are self-explanatory. It is seen (Table 2) that the error in these titrations does not exceed 2.5 per cent.

In some cases the titration curves of three ammonium salts taken together are of different nature, due to increase in concentration of electrolytes. Curve I (Fig. 2) shows the titration of a mixture of monoammonium phosphate, ammonium sulphate and diammonium phosphate; first the neutralization of monoammonium phosphate proceeds in the usual way, next diammonium phosphate is neutralized and finally ammonium sulphate reacts giving two or a single break depending upon the concentration of the solution. The titration curve of a mixture of monoammonium phosphate, diammonium phosphate and ammonium nitrate (Curve II, Fig. 2) is self-explanatory; all the ingredients give their breaks. The curve III (Fig. 2) shows the titration of a mixture of monoammonium phosphate, ammonium sulphate and ammonium nitrate: first two breaks are for monoammonium phosphate, the second two are for ammonium sulphate and the last is for ammonium nitrate. Some deviation from original nature of the titration curves [Curve-IV, (Fig. 2)] is observed in case of a mixture of diammonium phosphate, ammonium sulphate and

TABLE 2—CONDUCTOMETRIC TITRATION OF AMMONIUM SALTS AGAINST STANDARD CAUSTIC SODA WHEN TAKEN TWO AT A TIME (TOTAL DILUTION 100 ml.)

Mixture		Nos.	Estimation of (a)			Estimation of (b)		
			By Standard Method, mg.	By Conductometric Method, mg.	Error, %	By Standard Method, mg.	By Conductometric Method, mg.	Error, %
NH_4NO_3	$+ (\text{NH}_4)_2\text{SO}_4$	1	15.30	14.95	2.29	19.8	19.99	0.90
		2	28.40	29.68	0.90	9.90	9.72	1.9
		(a) (b)	3	15.30	15.10	1.10	9.90	10.02
								1.20
		1	9.85	9.70	1.50	28.4	29.05	1.95
		2	19.60	20.01	2.01	15.3	15.01	1.10
$\text{NH}_4\text{H}_2\text{PO}_4$	$+ \text{NH}_4\text{NO}_3$	1	9.85	9.75	1.01	15.3	15.24	0.85
		2	19.60					
		(a) (b)	3	9.85				
		1	15.3	15.60	1.96	19.60	20.12	2.58
		2	28.4	29.24	2.40	9.80	9.90	1.01
$(\text{NH}_4)_2\text{SO}_4$	$+ \text{NH}_4\text{H}_2\text{PO}_4$	1	9.90	9.80	1.01	9.85	9.75	1.01
		2	19.80	19.70	0.52	9.85	10.01	1.20
		(a) (b)	3	9.90	9.65	2.26	19.60	20.14
								2.01
		1	9.80	9.93	1.31	9.90	9.85	1.01
		2	19.75	19.60	0.94	9.90	9.70	2.01
$(\text{NH}_4)_2\text{HPO}_4$	$+ (\text{NH}_4)_2\text{SO}_4$	1	9.80	9.68	1.22	19.80	19.46	2.22
		2	19.75					
		(a) (b)	3	9.80				
		1	9.85	9.88	0.30	9.80	9.78	0.20
		2	19.60	19.28	1.12	9.80	10.66	2.60
(a) (b)		3	9.85	9.70	1.53	19.60	19.42	0.92

ammonium nitrate. The first break in this curve gives the reaction with diammonium phosphate where conductivity remains constant, after this conductivity decreases giving only one break for ammonium sulphate but when the neutralization of ammonium nitrate begins the conductivity again becomes constant until the complete reaction takes place. The results are given in Table 3; the error does not exceed 2.5 per cent which is quite satisfactory for such a complex system.

In order to test the applicability of this work in industrial analysis, some commercial fertilizers which contain two or more of the ingredients mentioned above were titrated by the present method, and the results compared with those obtained by available standard methods for their analysis. In case of commercial double salt which contains ammonium sulphate and ammonium nitrate, the titration curve in 20 per cent alcoholic medium is similar to the curve III (Fig. 1) corresponding to a mixture of pure ammonium sulphate and ammonium nitrate. Here also ammonium sulphate gives two breaks in dilute solution and one in concentra-

ted solution. The error in this case is within 1.6 per cent as compared with the result obtained by standard method of analysis (Table 4).

The titration curves of different nitrophosphate samples are given in Fig. 3. Curve I shows the titration of phosphonitric nitrophosphate sample A of 20-20-0 grade which contained monoammonium phosphate (but no diammonium phosphate) and ammonium nitrate, as the ammonium salts. The first break in the curve corresponds to the conversion of monoammonium phosphate to diammonium phosphate, the second break to the neutralisation of the produced diammonium phosphate and the third break to the neutralization of ammonium nitrate. Curve II (Fig. 3) shows the titration of phosphonitric nitrophosphate sample B of 20-20-0 grade which contained monoammonium phosphate, diammonium phosphate and ammonium nitrate as the ammonium salts. The first break corresponds to the conversion of monoammonium phosphate to diammonium phosphate, the second break to the neutralisation of the produced diammonium phosphate and that

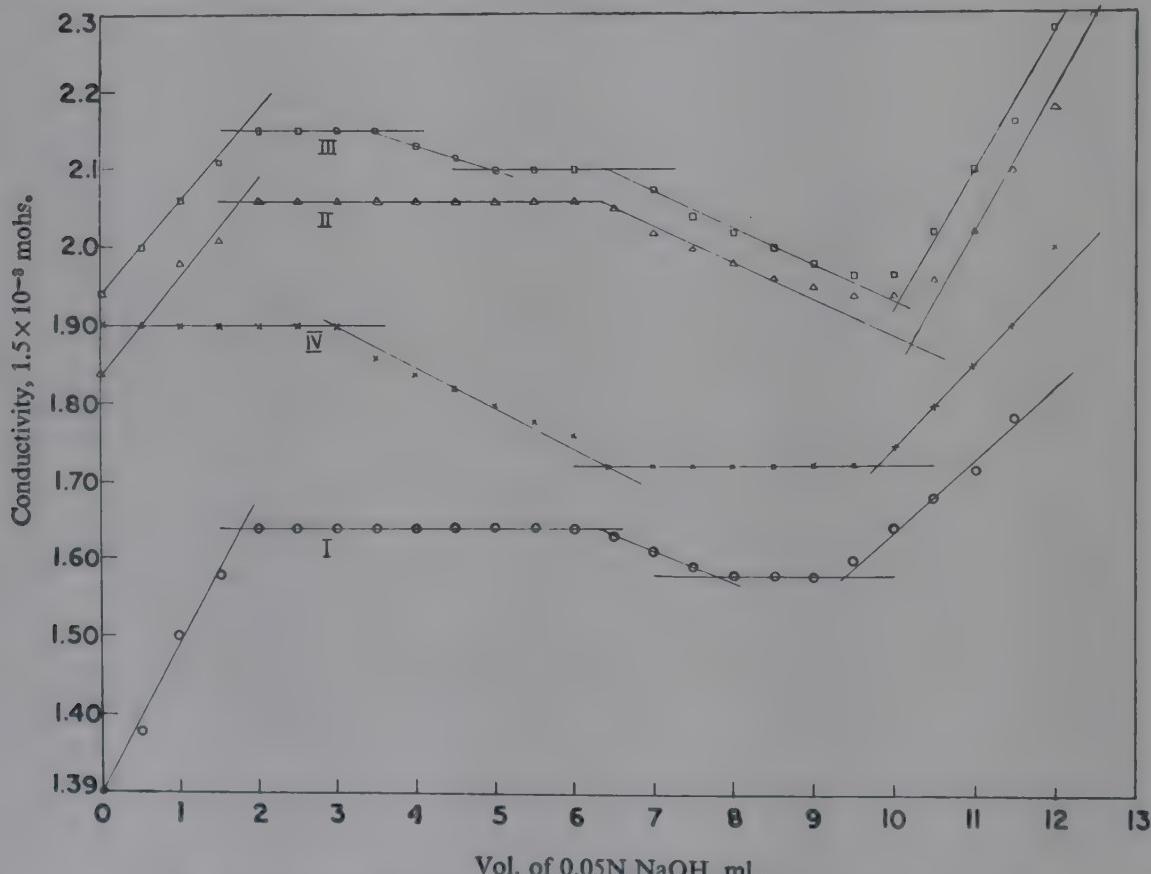


Fig. 2—Conductometric Titration of Ammonium Salts Taken Three at a Time

- I—5 ml. $\text{NH}_4\text{H}_2\text{PO}_4$ + 5 ml. $(\text{NH}_4)_2\text{HPO}_4$ + 5 ml. $(\text{NH}_4)_2\text{SO}_4$ Stock Soln. against 0.05N NaOH
- II—5 ml. $(\text{NH}_4)_2\text{HPO}_4$ + 5 ml. $(\text{NH}_4)_2\text{SO}_4$ + 5 ml. NH_4NO_3 Stock Soln. against 0.05N NaOH
- III—5 ml. $\text{NH}_4\text{H}_2\text{PO}_4$ + 5 ml. $(\text{NH}_4)_2\text{SO}_4$ + 5 ml. NH_4NO_3 Stock Soln. against 0.05N NaOH
- IV—5 ml. $(\text{NH}_4)_2\text{HPO}_4$ + 5 ml. $(\text{NH}_4)_2\text{SO}_4$ + 5 ml. NH_4NO_3 Stock Soln. against 0.05N NaOH

TABLE 3—CONDUCTOMETRIC TITRATION OF AMMONIUM SALTS AGAINST STANDARD CAUSTIC SODA WHEN TAKEN THREE AT A TIME (TOTAL DILUTION 100 ml.)

Mixtures	Nos.	Estimation of (a)			Estimation of (b)			Estimation of (c)			
		By Std. Method, mg.	By Con- ductome- tric Method, mg.	Error, %	By Std. Method, mg.	By Con- ductome- tric Method, mg.	Error, %	By Std. Method, mg.	By Con- ductome- tric Method, mg.	Error, %	
NH ₄ NO ₃ (a)	+ (NH ₄) ₂ HPO ₄ (b)	1	15.30	15.05	1.60	9.80	9.75	1.01	9.85	9.96	1.10
+ NH ₄ H ₂ PO ₄ (c)		2	28.40	29.62	0.85	9.80	9.68	1.22	9.85	10.01	1.60
NH ₄ NO ₃ (a)	+ (NH ₄) ₂ SO ₄ (b)	1	15.30	15.60	1.90	9.90	9.75	1.5	9.85	9.92	0.70
+ NH ₄ H ₂ PO ₄ (c)		2	28.40	28.20	0.85	9.90	9.80	1.01	9.85	9.70	1.53
NH ₄ NO ₃ (a)	+ (NH ₄) ₂ SO ₄ (b)	1	15.30	15.10	1.30	9.90	9.95	0.50	9.80	9.60	2.04
+ (NH ₄) ₂ HPO ₄ (c)		2	28.40	29.43	3.5	9.90	9.70	2.20	9.60	9.65	1.53
(NH ₄) ₂ HPO ₄ (a)	+ (NH ₄) ₂ SO ₄ (b)	1	9.85	9.94	0.90	9.90	9.80	1.01	9.85	9.69	1.63
+ NH ₄ H ₂ PO ₄ (c)		2	19.60	20.10	2.45	9.90	9.72	1.81	9.80	9.58	2.24

TABLE 4—CONDUCTOMETRIC TITRATION OF SOME COMMERCIAL FERTILIZERS WITH 0.05 N SODIUM HYDROXIDE IN AQUEOUS ALCOHOL (CONTAINING 20% ALCOHOL BY VOLUME) (TOTAL DILUTION 100 ml.)

Fertilizers	Stock Solutions: Double Salt				Nitrophosphate (Phosphonitric)		Nitrophosphate (by Sulphate Recycle)			
	Sam- ple No.	0.669 g./250 ml.			1.315 g./250 ml.		1.146 g./250 ml.			
		By Standard Method	By Con- ductome- tric Method	Total Ammoniacal Nitrogen, wt. %	By Std. Method	By Con- ductome- tric Method	Total Nitrate Nitrogen, wt. %	By Std. Method	By Con- ductome- tric Method	Water-soluble P ₂ O ₅ , wt. %
Double salt (ammonium sulphate nitrate)	1	19.94	19.80	0.74	7.40	7.52	1.60	—	—	—
	2	19.94	19.86	0.40	7.40	7.42	0.27	—	—	—
Nitrophosphate (phosphonitric) A	3	11.10	10.89	1.85	9.03	8.90	1.43	10.52	10.53	0.10
	4	11.10	10.85	1.90	9.03	8.85	1.98	10.52	10.60	0.58
Nitrophosphate (phosphonitric) B	5	12.10	11.93	1.40	9.03	8.90	1.43	14.28	14.55	1.80
	6	12.10	11.85	2.06	9.03	8.80	2.00	14.28	14.60	2.20
Nitrophosphate (obtained by sulphate recycle)	7	16.40	16.30	0.61	11.85	11.80	0.46	15.95	15.85	0.63
	8	16.40	16.25	0.92	11.85	11.95	0.84	15.95	16.10	0.93

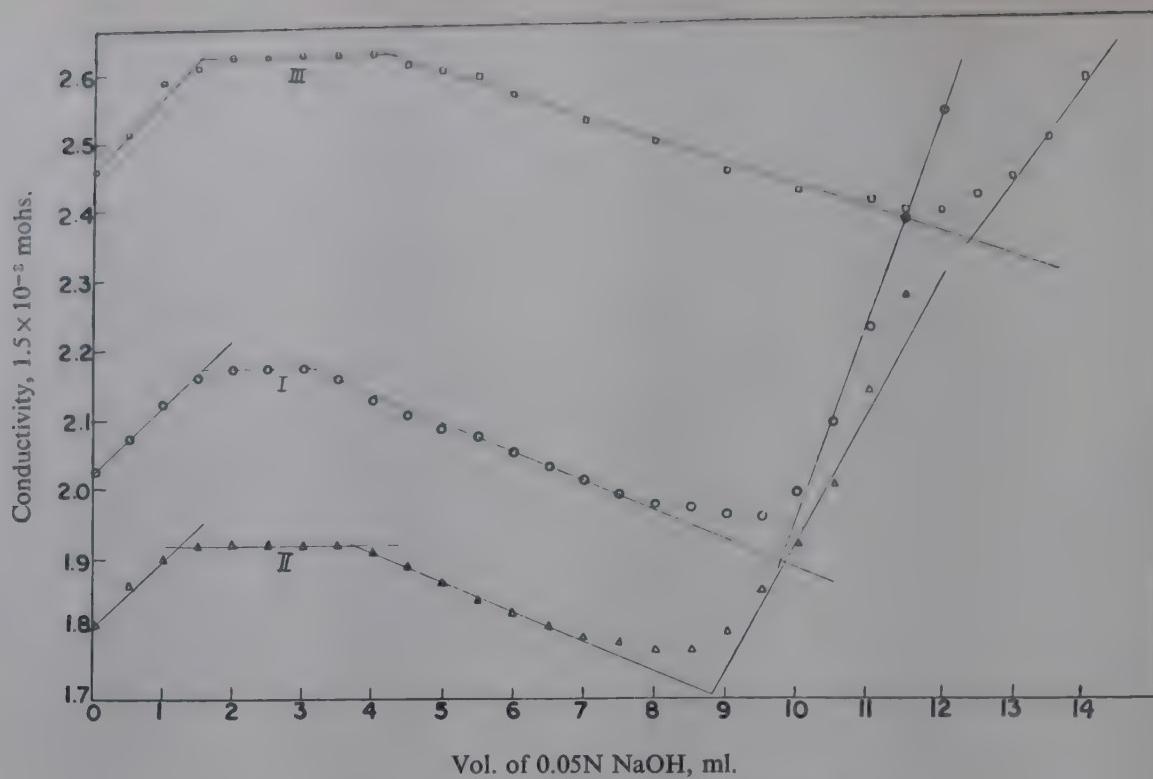


Fig. 3—Conductometric Titrations of Fertilizers

I—10 ml. Phosphonitic Nitrophosphate Stock Soln. against 0.05N NaOH
 II—7.5 ml. Phosphonitic Nitrophosphate + 2.5 ml. $(\text{NH}_4)_2\text{HPO}_4$ against 0.05N NaOH
 III—10 ml. Nitrophosphate (from Sulphate Recycle) against 0.05N NaOH

originally present, and the third break to the neutralisation of ammonium nitrate. Similarly, the curve III shows the titration of nitrophosphate (26-15-0) by the sulphate recycle process which contained monoammonium phosphate, diammonium phosphate and ammonium nitrate. The results obtained by conductometric titrations, as shown in Table 4, are in close agreement with those obtained by the standard methods. In this table the value of total ammoniacal nitrogen, corresponding to the different ammonium salts, and the water soluble phosphate, corresponding to mono or diammonium phosphate or both, have been compared.

Conclusion

The conductometric titration technique thus pro-

vides a reasonably accurate method for quick estimation of various ammonium salts when they are present, singly or in different mixtures in commercial fertilizers.

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Infrared and X-Ray Studies of Urea-Monocalcium Phosphate Complex

By

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An attempt has been made to study the mechanism of reaction between urea and monocalcium phosphate by x-ray and infrared spectroscopy. It has been suggested that the formation of oxygen to metal coordination bonds takes place in this complex and that urea replaces the water of crystallization of monocalcium phosphate in the process of formation of the same.

Urea is often used as a source of nitrogen in the manufacture of mixed N-P fertilizers. When it is mixed with superphosphate, a few problems may arise, one of which is its effect on the mechanical conditions and drillability of the mixture containing it. In a recent paper, Frazier¹ et al reported the formation of a new adduct in a mixture of urea and concentrated superphosphate which was identified as $4\text{CO}(\text{NH}_2)_2 \cdot \text{Ca}(\text{H}_2\text{PO}_4)_2$ that released water of hydration rapidly during storage forming a viscous saturated solution.

Since, urea is a desirable component of mixed fertilizers, a knowledge of the mechanism of reactions that may occur between urea and the monocalcium phosphate—the main constituent of superphosphate—is important to the understanding of the physical condition of the product. In view of these, the system urea-monocalcium phosphate monohydrate was studied by x-ray and infrared spectroscopy.

Experimental

Preparation of the Complex: The urea-monocalcium phosphate complex was prepared by following a nearly similar procedure described by Frazier¹ et al. A saturated aqueous solution of B.D.H. (Analar) quality monocalcium phosphate monohydrate was saturated with the same quality urea and filtered. The complex was obtained from the filtrate by adding a soluble calcium salt.

Dry mixture of the complex was also prepared by mixing urea with monocalcium phosphate monohydrate (less than 100 mesh) in the ratio of 4 moles to 1 in an agate mortar and kept at 30°C for two weeks.

The chemical analyses (Table 1) of the preparations were carried out by the usual methods.

I. R. Absorption Measurements: All the samples, viz. urea, monocalcium phosphate monohydrate, and both unheated and heated complexes were studied in the solid phase by KBr disc technique with the Perkin Elmer Infrared dual grating spectrophotometer, Model 421. KBr pellets were prepared following a procedure nearly similar to that by Ingebrigtsen² et al and described in an earlier paper³. The diameter of the pellet was 13 mm. having a thickness of 1 mm. The spectra was recorded from 2.5 to 18μ using a stripchart recorder, the scanning speed of which was 17 min. for the full range.

X-ray Measurements: The x-ray diffraction patterns of the samples, both freshly prepared and after heating to 110°C, were taken in a Guinier camera in the Philips X-ray unit, PW 1010. CuK α radiation was used, the x-ray tube running at 40 KV with 20 mA. The time of exposure was 6 hours to each sample. The intensities of lines on the x-ray powdered photographs were evaluated by visual estimation. The interplanar spacings were calculated with maximum accuracy and the phase

identifications were done by usual method of Hanawalt⁴ et al.

TABLE 1—ANALYSIS OF $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ COMPLEX

Sample No.	Composition, %			
	CaO	P_2O_5	$\text{CO}(\text{NH}_2)_2$	H_2O (diff.)
1. (Wet Process)	11.7	29.4	50.1	8.8
2. -do-	11.8	29.6	50.4	8.2
3. (Stoichiometric)	12.0	30.2	50.3	7.5

Results

X-ray Study: The x-ray diffraction data of the samples are shown in Table 2.

TABLE 2—X-RAY DATA OF UREA-MONOCALCIUM PHOSPHATE COMPLEX

Urea-Monocalcium Phosphate Complex	d Å	I	Urea-Monocalcium Phosphate Complex Heated to 110°C	d Å	I
	7.00	ms		4.70	vwv
	6.1	vw		4.00	vs
	5.39	vww		3.75	vw
	4.51	vww		3.61	vs
	4.42	w		3.46	m
	4.10	w		3.06	m
	3.99	vww		3.04	ms
	3.84	ms		2.95	vw
	3.80	m		2.82	vw
	3.65	m		2.72	vww
	3.59	s		2.65	w
	3.48	ms		2.53	ms
	3.42	s		2.42	m
	3.30	vww		2.34	w
	3.12	vww		2.14	ms
	3.05	w		2.02	vw
	2.95	vww		2.00	vw
	2.80	ms		1.84	ms
	2.57	vww		1.74	vww
	2.55	vww		1.72	vww
	2.52	vw		1.67	w
	2.50	vww		1.51	vw
	2.45	vww		1.37	vww
	2.42	vww		1.33	vw
	2.35	vww			
	2.27	vww			
	2.24	vww			
	2.20	w			
	2.15	vw			
	2.01	vww			
	1.86	vww			
	1.80	vww			
	1.74	vww			
	1.69	vww			
	1.67	vww			
	1.41	vww			

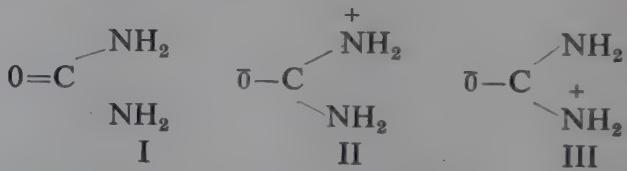
The x-ray analysis of the experimental sample, viz. urea-monocalcium phosphate complex, does not indicate the presence of either free urea or free monocalcium phosphate monohydrate as distinct separate phases. Recently, Frazier¹ et al have studied crystallographic properties of urea-monocalcium phosphate complex. Our results are in complete agreement with them.

The unit cell calculated from the patterns reported here is as follows: Urea-monocalcium phosphate—(a) = 5.69 Å (5.66); (b) = 21.60 Å (21.57); (c) = 7.40 Å (7.40); $\alpha = 90^\circ$; $\beta = 90^\circ 50'$ ($90^\circ 56'$); and $\gamma = 90^\circ$ (the values in brackets are those given by Frazier¹ et al).

Infrared Study: The absorption curves of urea, monocalcium phosphate monohydrate and urea-monocalcium phosphate complex are reproduced in Fig. 1.

The spectra of urea and monocalcium phosphate monohydrate, obtained in this study are quite similar to those reported by other workers^{5,6} and hence the assignments have been made accordingly. The wave numbers (cm^{-1}) of the absorption maximum together with their assignments are given in Table 3.

Interaction of Urea-Monocalcium Phosphate Monohydrate: The structure of urea involves resonance between the following three forms:



According to Penland⁵ et al, coordination of urea with metal ions can occur through nitrogen as well as oxygen atoms, and as a result of this coordination a change in many of the urea vibrations is expected to occur, which has been discussed in an earlier communication⁷.

The spectra of urea-monocalcium phosphate complex have considerable resemblance to those reported by Penland⁵ et al and indicate that oxygen to metal bonds are present in this system. The NH stretching vibrations observed in the spectra of the complex are almost at the same frequencies as those of urea. This suggests the relatively greater freedom of NH_2 groups in this complex. The band observed at 1640 cm^{-1} in the spectra of the phosphate complex can be assigned to NH_2 bending vibrations, the positions of which are relatively unchanged from those of free urea molecule. The infrared band observed at 1154 cm^{-1} in the spectra of the complex can be assigned similarly to NH_2 rocking vibrations. The CO stretching frequency appears around 1572 cm^{-1} , and the two bands observed at about 1480 and 1013 cm^{-1} may be assigned to the CN antisymmetric and symmetric

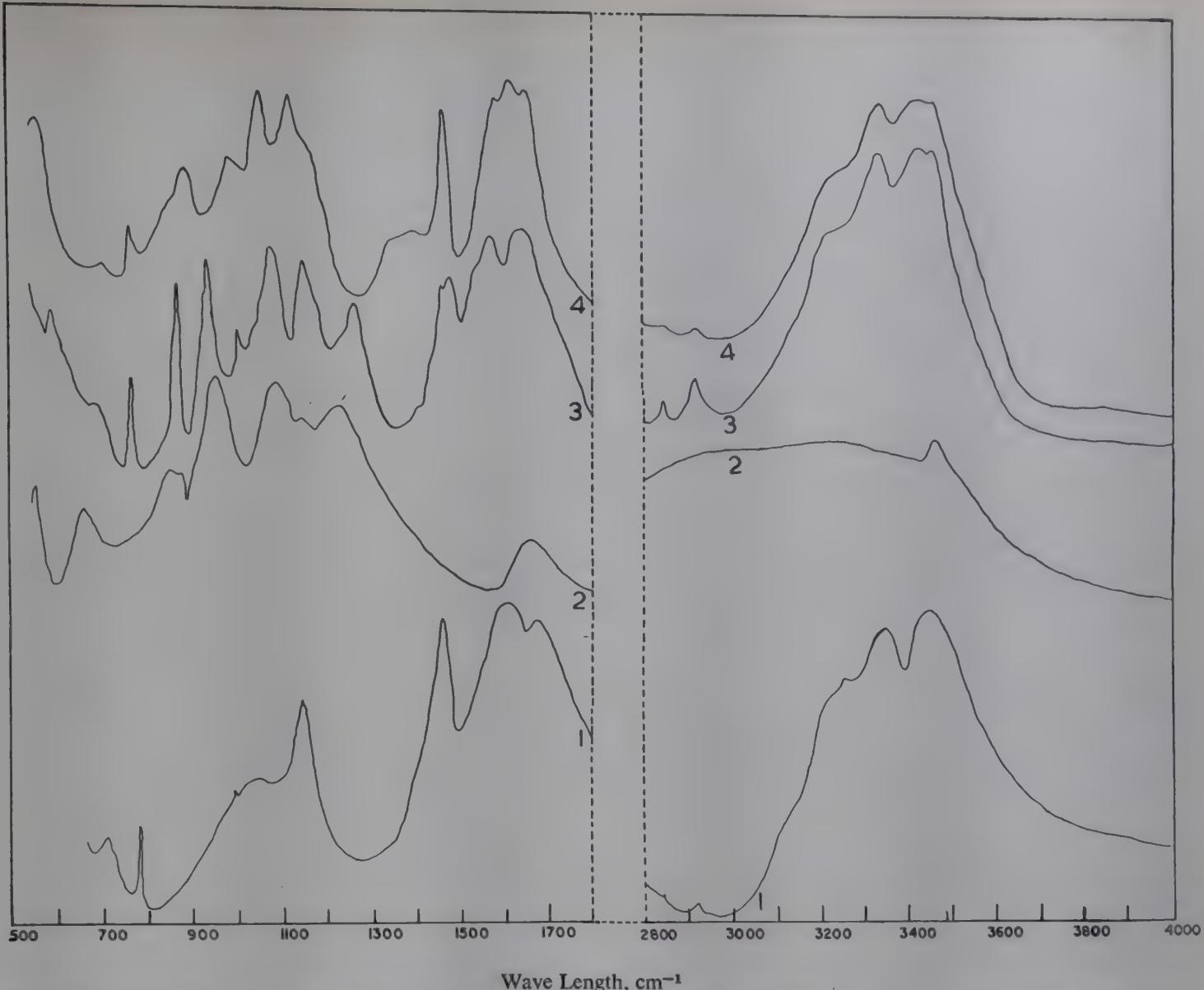


Fig. 1—Absorption Spectra of Urea, Monocalcium Phosphate Monohydrate, Urea Monocalcium Phosphate Complex and the Complex Heated to 110°C

1. Urea; 2. Monocalcium Phosphate Monohydrate; 3. Urea Monocalcium Phosphate Complex; 4. UMP Complex heated to 110°C

stretching frequencies respectively. This decrease in the CO stretching frequency and an increase in the CN stretching frequency from the corresponding frequencies of urea are expected because of the enhancement of the structures II and III due to coordination of metal ion through the oxygen of the urea molecule. A comparison of the main bands of the Cu (II)-urea complex of Penland⁵ et al with those of the urea-monocalcium phosphate complex indicates relatively good agreement.

General Discussion

The x-ray and infrared spectra of urea-monocalcium phosphate adduct when heated to 110°C reveals the presence of only two phases, viz. anhydrous monocalcium phosphate and urea indicating that it is unstable at that temperature.

It may be worthwhile to discuss here the role of the lattice water of monocalcium phosphate in the formation of the complex. The spectra of monocalcium phosphate monohydrate are different from those of the corresponding anhydrous salt, since the introduction of water molecules into the lattice changes the structure and the mode of packing. This results in a general shift of peaks to lower frequencies and is marked in the P-O stretching region. The P-O stretching frequency which normally occurs near 1300 cm⁻¹ in the anhydrous salt is decreased to 1220 cm⁻¹ in case of the hydrated salt; this is due to the formation of hydrogen bonding of the oxygen in the anion with the water molecules⁶. A comparison of the spectra of monocalcium phosphate monohydrate with its urea complex reveals a difference in the P-O stretching region. The P-O stretching fre-

TABLE 3—ABSORPTION MAXIMA IN cm^{-1} OBSERVED FOR UREA, MONOCALCIUM PHOSPHATE MONOHYDRATE, UREA-MONOCALCIUM PHOSPHATE COMPLEX AND THEIR ASSIGNMENTS

Urea†	Urea*	Assignments	Monocalcium Phosphate Monohydrate**	Monocalcium Phosphate Monohydrate††	Assignments	Urea-Monocalcium Phosphate Complex	Cu (II)-Urea Complex††	Assignments	Urea-Monocalcium Phosphate Complex	Heated to 110°C
3445 (s)	3445	NH_3 assym. stretching	3460 (m)	3425	H-O-H stretching modes	3453 (w)	3425	Free NH_3 stretching	3455 (w)	
3347 (s)	3343	NH_3 symm. stretching	3275	Combinations or overtones		3420 (s)	3340		3425 (s)	
3255 (ms)				3180		3330 (s)			3330 (s)	
1675 (s)	1683	NH_3 bending & CO stretching	1650 (s, b)	1650 (m)	H-O-H bending	3220 (sh)	3275		3225 (sh)	
	1629	NH_3 bending				2925 (w)			2925 (w)	
1610 (s)	1603	NH_3 bending & CO stretching				2845 (w)			2845 (w)	
1463 (s)	1471	CN stretching (antisymmetric)				1640 (s)	1640	NH ₃ bending and CO stretching for uncoordinated urea	1650 (s)	
						1620	1580	ν CO	1610 (m)	
						1480 (m)	1485	ν CN (antisymmetric)	1575 (m)	
1064 (w)	1005	CN stretching (symmetric)	960 (s)	980 (s, sh)	Ionic P=O stretching	1462 (w)	1470	$\text{P}=\text{O}$ stretching	1460 (s, sp)	
1000 (w)			880 (w)	963 (vs)	Ionic P=O stretching	1220 (m, sh)				
			850 (m)	913 (w)		1155 (w)	1154 (s)	Free NH_3 rocking	1126 (s)	
1152 (m)	1155	NH_3 rocking	1090 (s)	1090 (s, b)	Ionic P=O stretching	1150 (w)	1086 (s)	Ionic P=O stretching	1055 (s)	
						1090 (s)				
789 (ms)		δ (NCO)				980 (s, sh)	1010 (m)	ν CN (symmetric)	985 (m)	
718 (m)						963 (vs)	1015			
						913 (w)				
						890 (w)				
						880 (w)	878 (s, sp)	$\text{P}-\text{OH}$ bending	890 (m)	
						850 (m)				
							773 (m, sp)	763	770 (m)	
							695 (w)		705 (w)	
						670 (m)				

vs—very strong, s—strong, m—medium, w—weak, b—broad, sp—sharp, and sh—shoulder
 †KBr pellet spectrum obtained by the authors. Assignments made in accordance with observation by Penland⁶ et al.
 *Taken from Penland⁶ et al.
 ‡KBr pellet spectrum obtained by the authors. Assignments made in accordance with observation by Corbridge and Lowe.⁶
 **Taken from Corbridge and Lowe.⁶
 †† Taken from Penland⁶ et al.

quency in the complex appears at 1280 cm^{-1} , and the P-OH bending frequency which splits into two bands at 880 and 850 cm^{-1} in the monocalcium phosphate monohydrate appears as a strong single peak at 878 cm^{-1} in the complex. This probably indicates the absence of the water of crystallization in the complex.

Further, the principal water bands in inorganic hydrates are generally found at 3550 - 3200 cm^{-1} (antisymmetric, ν_3 and symmetric, ν_2 modes) and 1630 - 1600 cm^{-1} (H-O-H bending mode, ν_3). In monocalcium phosphate monohydrate, the occurrence of the bands at 3425 , 3180 and 1650 cm^{-1} have been reported⁶. The peaks appearing at 3420 and 1650 cm^{-1} in the urea-monocalcium phosphate complex may be due to water bands, but it is more likely that they arise from the NH_2 stretching and bending modes of urea respectively, since these peaks did not disappear even when the samples of the complex were heated above 100°C . The 3445 cm^{-1} band of urea splits into two bands at 3453 and 3420 cm^{-1} due to interaction of NH_2 groups with hydroxyl of $(\text{H}_2\text{PO}_4^-)$ -ion. These results indicated that probably urea replaces the water of crystallization of monocalcium phosphate to form the complex. This is further corroborated by the fact that anhydrous monocalcium phosphate does not form the complex¹. This

establishes the earlier observation on the formation of this complex that "urea reacts with monocalcium phosphate monohydrate in the presence of moisture to set free the water of hydration of the latter and form the complex"¹.

Acknowledgements

The authors' thanks are due to Dr. B. K. Banerjee, Addl. Superintendent, for his interest and helpful suggestions, and to Mr. K. C. Banerji, Deputy Superintendent, for his criticisms and discussions during the course of this investigation.

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Infrared Absorption Study of Cobaltic Biuret Complex

By

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The infrared absorption spectra of cobaltic biuret complex, $\text{K}_3[\text{CO}(\text{NHCONH})_3] \cdot 2\text{H}_2\text{O}$ have been observed. The behaviour of the bands around 6μ and 3μ regions indicate that the formation of the complex between biuret and cobaltic ion occurs through the nitrogen of end-NH groups of biuret molecule and the complex biuret molecule has a *cis*-configuration.

Introduction

Biuret, which is present in almost all fertilizer-grade urea, is known to form chelate complexes with metal ions and this complex formation subsequently serves

as a method for the estimation of biuret^{1,2} itself. Sanyal³ et al reported that biuret can be estimated successfully by forming a coloured complex with a cobaltic salt. Crystallographic properties of this complex have also been determined in this laboratory by Ghosh et al.⁴

Most of the structural determinations of metal biuret complexes by x-ray and infrared spectroscopy⁵⁻⁶ have been confined to bivalent metal ions only. No structure determination has yet been reported for trivalent metal complexes with biuret. The present investigation was undertaken with a view to ascertain the mode of coordination of biuret with trivalent metal ion, which is necessary in order to evaluate the physical properties of the complex.

Experimental

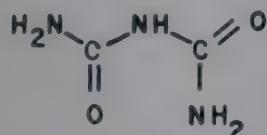
The complex was prepared according to the previous method³. The samples, viz. biuret and the cobaltic biuret complex, were studied in the solid phase by potassium bromide disc technique using the Perkin Elmer infrared dual grating spectrophotometer, Model 421.

Potassium bromide pellets were prepared by a procedure¹⁰, nearly similar to the one adopted by Ingebrigtsen et al¹¹. The diameter of the pellet was 13 mm. having a thickness of nearly 1 mm. The spectra were recorded from 2.5 to 18 μ using a strip chart recorder having a scanning speed of about 17 minutes for the full range.

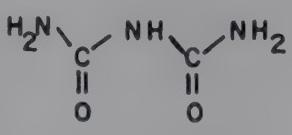
Results and Discussion

The infrared spectra of biuret and its complex with cobaltic ion are reproduced in Fig. 1, and the observed frequencies with probable assignment shown in Table 1.

Biuret molecule is known to exist in two configurations, viz. *trans*- and *cis*- forms as shown below



TRANS-FORM



CIS-FORM

A

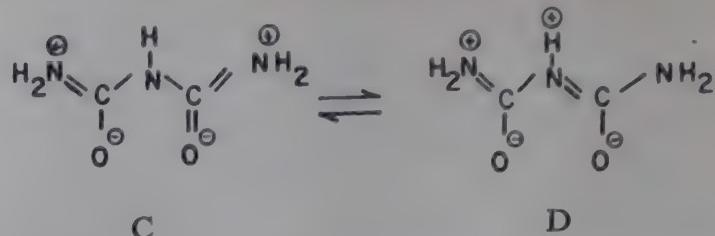
B

and these can be distinguished by their characteristic infrared spectra⁷.

Earlier observations have shown that in neutral solutions metal ions are coordinated to biuret molecules through nitrogen as well as oxygen atoms while in alkaline medium metal ions are coordinated through the nitrogen atoms.

Like urea, if the biuret molecule is considered to have the following resonating structures then coordination

through oxygen atoms would result in a decrease of



C=O stretching and an increase in the C—N stretching frequencies. Coordination through nitrogen would not be expected to result in significant changes in carbonyl stretching frequency compared with that of free biuret molecule although some effect due to change in configuration from *trans*- to *cis*- might be expected.

A comparison between the characteristic infrared absorption bands of biuret and the cobaltic complex (Table 1) reveals that biuret molecule before coordination exists in *trans*-configuration and after coordination to cobaltic ion in *cis*-configuration.

The infrared spectra of the complex (Fig. 1) did not show any significant changes in the carbonyl stretching frequency compared with that of biuret although some of the bands are modified by the influence of coordination and change in the configuration from *trans*- to *cis*- . The 6 μ region shows minor changes in intensity and position of the biuret vibrations. The band at 1693 cm⁻¹ probably arises from the water of crystallization. X-ray analysis of the cobaltic biuret complex also confirms the presence of the water of crystallization in it⁴. The rest of the spectrum is almost identical with that of biuret.

The above observation indicates that biuret molecules are coordinated to cobaltic ion through nitrogen atoms of the end NH groups. Further, the general similarity of the spectra of the complex with that of the sodium bis (biureto) cuprate tetrahydrate⁸ also supports the above view, and accordingly tentative assignments for various vibrations of the complex (Table 1) have been made by analogy to the latter.

The formation of nitrogen to metal bonds between biuret molecules and the metal ion should bring about pronounced change in the 3 μ region. The free NH stretching frequency at 3400 cm⁻¹ in biuret is absent in the complex and replaced by two broader bands at 3380 and 3185 cm⁻¹. The vibration at 3380 cm⁻¹ is analogous to that of amide type NH stretching modes and is expected to occur if the NH₂ groups of biuret are replaced in these complexes by NH groups. Therefore the band at 3380 cm⁻¹ in the complex can be assigned to this vibration.

TABLE I—ABSORPTION MAXIMA IN cm^{-1} OBSERVED FOR BIURET AND COBALТИC BIURET COMPLEX AND THEIR ASSIGNMENTS

<i>Trans</i> -Form	Biuret*	<i>Cis</i> -Form	Biuret†	Cobaltic Biuret Complex [K_3 (Co-(NH CO NH CO NH) ₃] 2H ₂ O	Assignments	$\text{Na}_2[\text{Cu}(\text{NH CO NH CO NH}_2)]^{**}$ 4H ₂ O
	3500 Sh, bd					
	3465 S		3460			
3400 S		3402 vs	3400		ν NH (Coordinated)	3370 w
				3380 bd		
3220 s, bd		3250 s, bd	3230	3185 bd	ν NH (Imide type)	3320 s
3020 w, sh			3015			3220 s
				2915 w		3050 w
		2820 vw	2860	2845 w	2×1444	2890 w
			2020 vw			2560 w
1740 s				1693 bd		
1710 vs	1725 vs		1706 vs		δ OH (Water of crystallization)	1700 bd
	1683 vs			1672 ms	δ C=O (Out of phase)	1655 s
	1622 s					
1600 s	1585 s			1596 s	ν C=O (In phase)	1590 s
	1495 m					
1411 m	1422 s		1412 m	1444 s	ν CN (In phase)	1460 s
1356 m	1326 vs		1359 m	1378 s	ν CN (Out of phase)	1375 s
						1253 s
1124 w	1132 w		1124 w	1142 w	δ NH (Coordinated)	1235 s
1090 w	1077 m		1093 w	1080 w		1150 w
				1055 m		
				1032 w		
				1010 m		
952 w	945 w		950 w	940 vs	δ CN (In phase)	975 w
				878 m		
				859 w		
800 w	795 w		797 w			
	775 m					775 m
765 m	764 m		764 m		π NH (Imide type)	763 m
						745 m
738 m						
706 m	714 m		708 m	700 m	δ C=O	
	675 w		611 w	668 m		
				610 m	δ (NCO)	

*—Taken from K. Aida⁷; **—Taken from K. Aida⁸ et al; †—KBr pellet spectrum obtained by authors; vs—Very strong; s—Strong m—Medium; w—Weak; sh—Shoulder; vw—Very weak; bd—Broad; ν—Stretching; π—Out of plane deformation; δ—In-plane, deformation.

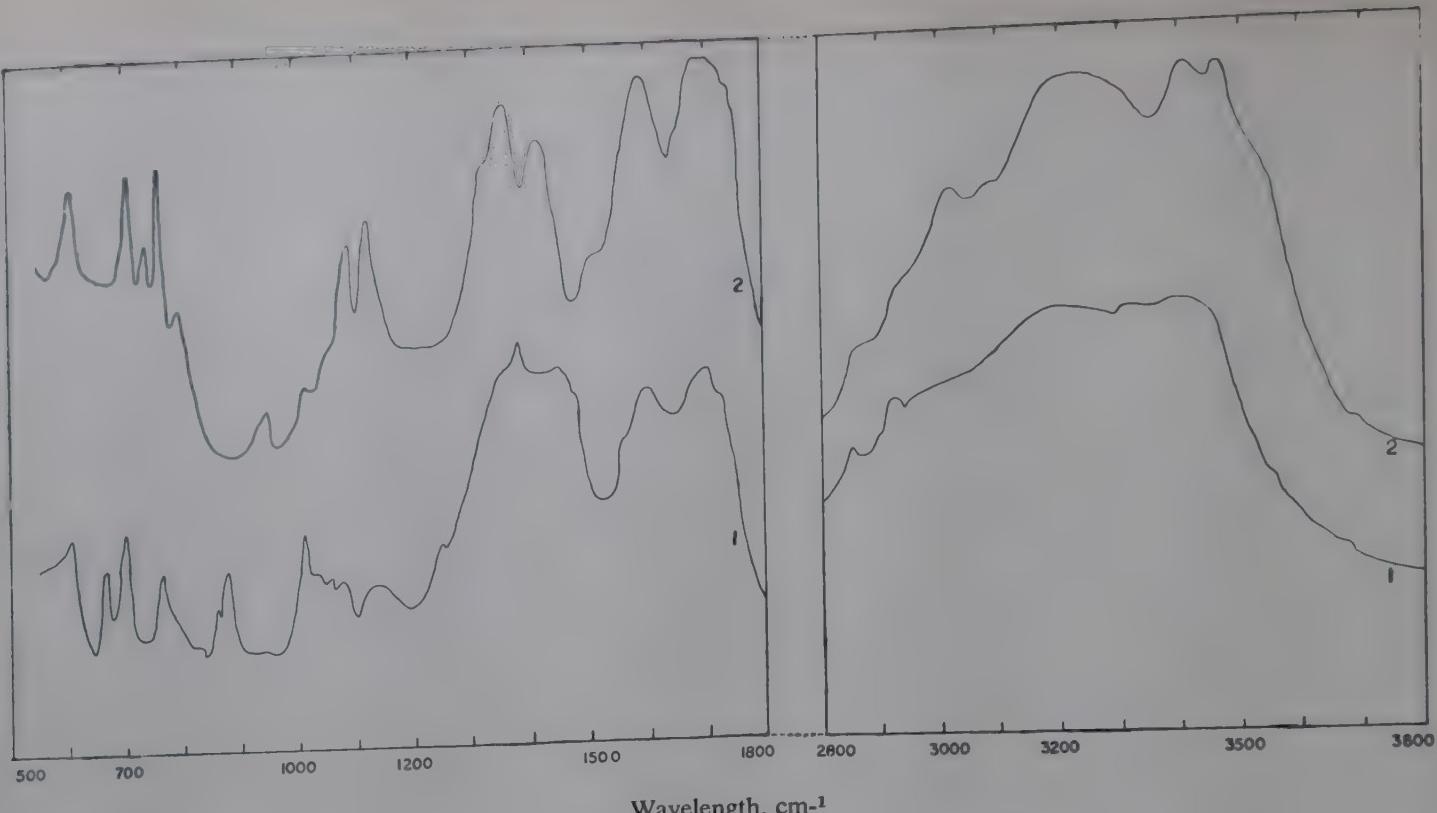
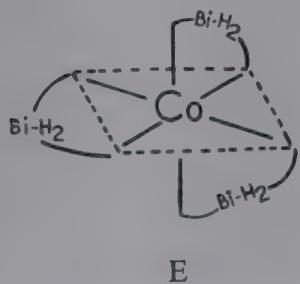


Fig. 1—Infrared Spectra of Biuret and Its Complex
1. Cobaltic Biuret Complex
2. Biuret

The NH stretching frequency in cyclic imides and related products generally occurs⁻¹² at about 3200 cm⁻¹. The band at 3185 cm⁻¹ in the complex may, therefore, be considered to arise from central imide type of NH group (E) which is analogous to cyclic imides.

Considering the above observations, the structure of the complex may therefore be written as



The conclusion is consistent with the postulated structure of the cobaltic biuret complex derived by spectrophotometric and conductometric study of the complex formed by the reaction of hexamine cobalt chloride with biuret at pH 1.6¹³.

Acknowledgements

The authors' thanks are due to Dr. B. K. Banerjee,

Additional Superintendent, for his interest and helpful suggestions and to also Sri K. C. Banerji, Deputy Superintendent, for helpful criticism and discussions during the course of this investigation.

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Infrared Spectra of Mineral Apatites

By

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The infrared absorption spectra of samples of apatites are given. The frequencies and assignments of the bands for 17 mineral apatites from different localities are provided. The OH-band at 3578 cm.⁻¹ was absent or very weak in many apatites. This may be due to the high fluorine or chlorine contents of the minerals.

In recent years there has been increasing interest in infrared application to mineral apatites¹⁻²⁹. Mineral apatites occur as minor constituents of many igneous rocks and are also found in crystalline limestones. Less well crystallized apatites (rock-phosphate or phosphorite) occur in large deposits²¹.

The mineral specimens for this investigation were made available from the collections of the United States

National Museum. Infrared spectra were recorded with a Beckman Infrared Spectrophotometer IR-12. An automatic filter device was conducted with the instrument and was divided as follows: 200-300 cm.⁻¹ (Filter No. 1), 300-510 cm.⁻¹ (Filter No. 2), 510-783 cm.⁻¹ (Filter No. 3), 783-1110 cm.⁻¹ (Filter No. 4), 1110-1872 cm.⁻¹ (Filter No. 5), 1872-2923 cm.⁻¹ (Filter No. 6), and 2923-4000 cm.⁻¹ (Filter No. 7). Samples were prepared as KBr or CsI pellets by pressing under vacuum at 20,000 to 25,000 pounds per square inch in a KBr steel die. A blank KBr or CsI disc was used in the reference beam to compensate for energy loss resulting from KBr or CsI in the sample beam.

TABLE 1—SPECIMENS OF MINERAL APATITES FROM VARIOUS LOCALITIES

Locality	U.S. National Museum Catalogue Number
1. Hugo Pegmatite (Keystone) South Dakota, USA	R9481
2. Wilberforce, Ontario, Canada	R14068
3. Kukisvumchorr deposit, Kola Peninsula, USSR	103493
4. Odegaard, Bamle, Norway	R7169
5. Odegaard, near Feset, Norway—Chlorapatite	114937
6. Cherokee Co., Georgia—hydroxyapatite	106217
7. Harts Range, Northern Territory, Australia	R10443
8. Schwartzenstein, Tyrol, Austria	82049
9. Llallagua, Bolivia	103869
10. San Diego, California, USA	R15184
11. Schlaggenwald, Bohemia, Czechoslovakia	R5214
12. Laurel Creek Mine, Rabun Co., Georgia, USA	49065
13. Greifenstein, Saxony, Germany	82421
14. Buckfield, Maine, USA	94750
15. Cerro Mercado, Durango, Mexico	104021
16. Franklin, New Jersey, USA	R5221
17. Khibina, Kola Peninsula, USSR—Saamite	113855

The apatites with their localities and catalogue number of U.S. National Museum are given in Table 1. The chemical analysis of a few of them was known and is presented in Table 2. The frequencies for the infrared absorption bands of these mineral apatites are given in Table 3. A number of the poorly crystallized apatites had a water absorption band but the hydroxyl band at 3578 cm.⁻¹ was absent or very weak. The absence of this OH⁻ group frequency is due to the high fluorine content of the mineral apatites. The ionic radii of OH⁻ (1.53 Å) and F⁻ (1.36 Å) are very close together and fluorapatite has the same atomic arrangement as hydroxyapatite but with the F⁻ groups in the hydroxyl positions (though F⁻ groups may not be located precisely in the OH⁻ positions). The OH⁻ ions of hydroxyapatite lie with their internuclear axes coincident with the sixfold screw axis²⁶. The absence of 3578 cm.⁻¹ OH⁻ band shows that most of the positions on the sixfold screw axis are now occupied by F⁻ rather than OH⁻ ions. The assignments of the important frequencies are given in Table 4.

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TABLE 2—CONSTITUENTS OF APATITES

Constituents	Cerro Mercado, Durango (Mexico)	Kukisvumchorr, Kola Peninsula (USSR)	Constituents	Khibina, Kola Peninsula (USSR) Saamite	Odegaard, near Feset (Norway)	Wilberforce Ontario (Canada)
F	3.27	3.24	CaO	42.38	52.97	55.16
Ca	40.5	38.6	MnO	0.05	—	0.12
P	18.6	18.0	P ₂ O ₅	38.33	40.50	41.30
CaO/P ₂ O ₅	1.33	1.31	SrO	11.42	—	—
			SiO ₃	1.55	1.16	—
			MgO	0.05	0.29	—
			Fe ₂ O ₃	0.12	0.18	0.63
			FeO	—	—	0.14
			Al ₂ O ₃	0.34	—	0.24
			F	3.73	0.17	3.67
			Na ₂ O	0.13	0.22	—
			K ₂ O	0.07	0.10	—
			H ₂ O	0.28	—	0.01
			CO ₂	—	—	0.50
			Cl	—	4.13	0.07
			Insoluble	—	—	0.28

TABLE 3—FREQUENCIES (cm⁻¹) FOR ABSORPTION SPECTRA OF MINERAL APATITES

Apatite No 1	2	3	4	5	6	7	8	9
245 w	250 w	255 w	245 vw	262 w	250 m	260 w, br	245 sha, m	245 sha, m
280 w	290 w	285 vw	305 m	315 vw	345 m	315 w	280 w	280 sha, m
325 w	320 vw	325 vw	355 m	422 vw	415 vw	360 w	339 w	325 m
420 w	442 vw	415 vw	425 vw	475 w	475 w	428 vw	352 sho	350 vw
480 w	475 w	475 w	475 w	575 s	572 s	470 w	440 vw	425 vw
578 s	578 s	578 s	575 s	608 s	605 s, sha	578 m	475 w	475 vw
605 s	605 s	605 s	605 s	668 vw, sha	635 m	605 m	582 w	578 m
670 vw, sha	862 vw	668 vw, sha	680 vw	963 vw	965 w, sha	678 vw	608 m	602 m
965 vw	962 w	745 w	725 w	1045 m	1045 s	735 m, br	680 vw	655 vw
1045 s	1042 s	965 w	965 w, sha	1085 w	1095 s	870 sho	725 vw	968 vw
1095 w	1095 s	1045 s	1045 s	1385 w	3585 vw	965 w	965 sha, w	1045 m
1390 w	1430 w	1430 w	1095 m			1040 m, br	1050 s	1075 sho, vw
1630 vw	1455 w	1458 w	1385 vw			1095 w	1100 w	1095 w
3440 vw			2860 vw			1415 vw	1410 vw	1262 w
			2940 w			1435 vw	1445 vw	1630 vw
						1468 w		3440 vw
						2010 vw		
						3550 w		
10	11	12	13	14	15	16	17	
245 sha, m	245 sha, m	250 w	250 sha, m	245 w	285 w	245 m	245 sha, m	
280 w	285 m	270 w	282 sha, m	285 vw	325 w	280 m	275 w	
339 w	328 m	320 m	325 m	335 vw	435 vw	325 m	320 w	
352 sho	430 w	355 w	430 vw	435 vw	475 w	430 vw	420 vw	
440 vw	470 w	435 vw	470 m	475 w	572 s	472 w	470 m	
475 w	575 s	475 w	578 s	570 w	608 s	578 s	578 s	
582 w	605 s	585 w	605 s	575 w	968 s	602 s	605 s	
608 m	670 sha, w	612 m	965 sha, w	605 w	1045 s	668 sha, w	670 sha, vw	
680 vw	965 vw	675 vw	1045 s, br.	670 sha, vw	1098 s	715 w	965 vw	
725 vw	1045 s	730 vw	1095 m	960 vw		865 vw	1045 s	
965 sha, w	1098 s	745 vw	2000 w	1040 w, br.		875 vw	1075 w	
1050 s	1630 br.	885 vw		1100 vw		965 sha, w	1430 vw	
1100 w	3440 s, br.	965 w		2000 vw		1042 s	1460 vw	
1410 vw		1050 s				1078 sho		
1445 vw		1095 s				1095 m		
		1625 br.				1432 w		
		1640 br.				1458 w		
		3540 br.				2000 w		

w=weak; vw=very weak; sho=shoulder; sha=sharp; s=strong; br=broad; m=medium

TABLE 4—ASSIGNMENTS OF THE INFRARED FREQUENCIES
OF MINERAL APATITES

Frequency (cm.--) near or at	Assignment
3578	ν_3 OH
1470	ν_1 CO ₃ in-plane stretching
1420	ν_4 CO ₃ asymmetric stretch
1630	O-H bending, water
1080	ν_3 PO ₄
1040 }	
865	ν_2 CO ₃ out-of-plane deformation
712	CO ₃ in-plane deformation
980	ν_1 PO ₄
635	ν_L OH
363	ν_2 PO ₄
515	ν_4 PO ₄
430	$\nu_3 - \nu_4$, 1040-605=435
470	$\nu_3 - \nu_4$, 1045-575=470

Acknowledgements

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Some Studies on Shelf Sediments from the Western Coast off Bombay and Ratnagiri

By

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This paper describes physical and mineralogical investigations on some grab samples of undersea mud off Ratnagiri and Bombay, collected by an expedition conducted jointly by the Bhabha Atomic Research Centre and the Maharashtra State Fisheries Department in 1964 and 1966. Illite has been found to be the dominant clay constituent of these sediments. Aragonite forms the bulk of the inorganic carbonates in some samples while the organic fractions consist of foraminifera and mollusks. These studies were directed to account for the increased values of dissolved phosphate in the sea water, as determined during the earlier expeditions, but no factors could be traced correlating these values with the P_2O_5 distribution in the sediments. The paper further discusses at length the possibilities of undersea phosphoria formation in and around the region.

In November-December 1964, an expedition¹ was led to Angria Bank jointly by the Bhabha Atomic Research Centre, Trombay, and the Maharashtra State Fisheries Department with a view to study the hydrography of the bank and explore the fishery potential of the area. This bank is located in the Arabian Sea, off Ratnagiri ($16^{\circ} 59' N$; $73^{\circ} 16' E$) and is outside the continental shelf. The shallow bank with an average depth of 15 fathoms has a coralline bottom and sides sloping abruptly towards the sea. The channel between the shelf and bank is ten miles wide and, on an average, 150 fathoms deep. Hydrographic data obtained during the 16 days' cruise in the region revealed relatively high values of dissolved oxygen and inorganic phosphates in the vicinity of the bank. Subsequently in March, 1966, another expedition² was led in the coastal waters north of Bombay.

During these two expeditions several mud samples were collected from the sea bottom, of which 19 sediment samples, (Table 1, Fig. 1) (12 from first expedition and 7 from second) were obtained* by the authors for mineralogical investigations. Their faunal content were also investigated. This study was aimed at, primarily, to account for the higher content of dissolved

inorganic phosphates in the coastal waters and to find whether the off-shore marine deposits, in and around the region, had something to do with it.

TABLE 1—LIST OF STATIONS FOR SEDIMENT SAMPLES

Period of Collection: J. series 21-11-64 to 6-12-64
TR-series 21-3-66 to 28-3-66

Sl. No.	St. No.	Latitude	Longitude	Depth
1.	TR-6	$19^{\circ}55.4'N$	$72^{\circ}28.3'E$	—
2.	TR-10	$19^{\circ}47.2'N$	$72^{\circ}37.3'E$	—
3.	TR-11	$19^{\circ}44.9'N$	$72^{\circ}36.4'E$	—
4.	TR-13	$19^{\circ}39.5'N$	$72^{\circ}33.4'E$	—
5.	TR-14	$19^{\circ}43.8'N$	$72^{\circ}28.5'E$	—
6.	TR-16	$19^{\circ}46.9'N$	$72^{\circ}34'E$	—
7.	TR-18	$19^{\circ}50.0'N$	$72^{\circ}34.2'E$	—
8.	J-4	$18^{\circ}25'N$	$71^{\circ}47'E$	80M
9.	J-5	$17^{\circ}56'N$	$71^{\circ}59'E$	88M
10.	J-30	$16^{\circ}50'N$	$72^{\circ}44'E$	70M
11.	J-32	$16^{\circ}59.5'N$	$73^{\circ}10'E$	31M
12.	J-34	$17^{\circ}07'N$	$72^{\circ}57'E$	45M
13.	J-40	$17^{\circ}58'N$	$72^{\circ}06'E$	88M
14.	J-43	$18^{\circ}36'N$	$72^{\circ}05'E$	70M
15.	J-44	$18^{\circ}40'N$	$72^{\circ}14'E$	64M
16.	J-45	$18^{\circ}49'N$	$72^{\circ}33'E$	32M
17.	SH-1	$18^{\circ}26.5'N$	$72^{\circ}37'E$	—
18.	SH-3	$17^{\circ}32'N$	$72^{\circ}55'E$	—
19.	SH-4	$17^{\circ}07'N$	$73^{\circ}08'E$	—

*Through the courtesy of Dr. A. K. Ganguly, Health Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay.

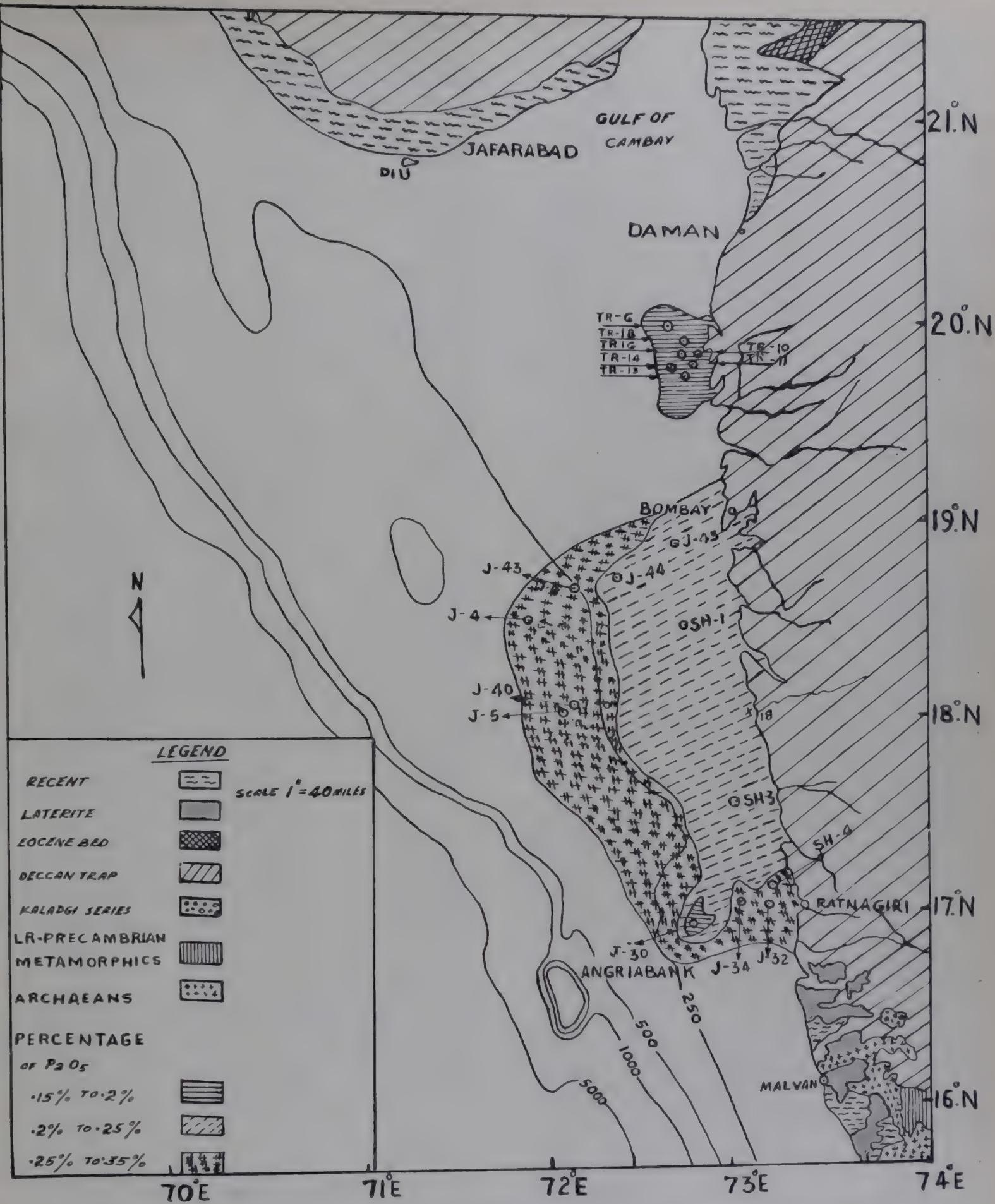


Fig. 1—Generalized Geological Map of the Area Showing Off-Shore Distribution of Phosphate and Location of Stations

Physiography, Areal Geology of the Bordering Land and Climatic Conditions

Topographically, the bordering land of the sea in question can be broadly divided into three divisions, viz. (a) the coastal strip with small creeks and harbours, (b), the central hilly belt mostly made up of the monotonous Deccan trap and laterite as in the Malvan area (Fig. 2), considerably dissected by numerous tributary streams thereby rendering the topography with complexity, and (c) the steep wall-like ridges of *Sahydris* which is the most dominant topographical feature, separating the eastern region from the rest.

In the Ratnagiri area, most of the rivers originate in the *Sahydris* and the connected spurs and run through the deep narrow valley. The river *Vaghotan*, reaching the Arabian sea at Vizaydrug ($16^{\circ}33'$; $73^{\circ}23'$), constitutes an important drainage system of the area. There are two other rivers; one, *Gad*, flowing into the sea north of Malvan ($16^{\circ}4'$; $73^{\circ}30'$) and the other *Karli*, flowing through the *Karli* creak. All these traverse a very rugged terrain and are dissected by innumerable tributaries.

Starting from Daman in the north, ($20^{\circ}27'$; $72^{\circ}50'$) to Vizaydrug in the south, ($16^{\circ}33'$; 73°) the entire length facing the Arabian sea is occupied by the monotonous sequence of Deccan trap. To the north of Daman, the coastal strip is occupied by alluvium. The central hilly terrain in the Ratnagiri district is made³ up of the Deccan trap, Konkan-laterite and some exposures of Kaladgi series of the Cuddapah age consisting of both metamorphic group and arenaceous group of sedimentary rocks. The metamorphic group includes phyllite, mica schist and biotite-garnet granulites, while the sedimentaries include sandstone and conglomerate. To the east of Malvan, quite a large tract of the area is occupied by unclassified granites of the Archaen age. Besides the above, basic intrusives like dolerite, olivine dolerite, olivine gabbro, picrite and chromite-serpentine rocks and acid intrusives like biotite-hornblende granite, coarse porphyritic granite and pegmatite are not uncommon in the area. The regional distribution of the different rocks can be seen in the geological map (Fig. 2).

The depositional environment has got a direct bearing with the climatological variation, as it can be effected by the circulation in the off-shore areas as well as by transportation of sediments by the agencies of wind and water from the bordering lands to the sea. In fact, the heavy rainfall of about 200 cm./year mainly from May to September in the elevated coastal strip results in a large run-off into the sea.

Sediments

In a broad sense the sediments collected from all the stations show certain homogeneity in their nature. The overall colour of the samples varies from olive grey (J-30), light brownish grey (TR-13), to light snuff grey. It may be mentioned in this connection that some depositional conditions are reflected in the colour of the sediments. But in the present case, the colour factor was not significant enough to show either the depositional environment or the source areas from where the sediments were derived.

Mechanical analyses (Table 2) were carried out for 11 samples following the method by Piper⁴. Fig. 2 gives the graphic representation of the size fractions of clay, silt, fine sand and organic material determined by pipette analysis. In all the samples, the silt percentage varies from about 7 to 25 per cent without forming any mode. In 9 out of the 11 samples, the percentage of clay is high, which points to the poor washing characteristics and deposition in a calm and quiet environment. The other two samples show a good percentage of organic matter indicating an agitated water environment. A few samples belonging to the J-series show poor sorting, while the sediments belonging to the TR-series are fairly well sorted. Microscopic examination of the fine sand fraction reveals that the grains are sub-angular to sub-rounded, while a few grains show perfect faces. In the lighter fraction, quartz is the most predominant constituent, and sometimes makes up about 60 per cent of this fraction. Among the feldspars, plagioclase is conspicuous. In some samples collected from the Stations J-30 and J-32, slight increment is noticed in the K-feldspar

TABLE 2—MECHANICAL ANALYSES OF THE SEDIMENTS

Sample	Clay %	Silt %	Fine Sand %	Coarse Sands %	Carbonate and organic matter %
TR-11	64.32	18.48	0.30	Absent	16.87
TR-13	65.24	25.48	Negligible	"	9.00
TR-16	55.60	18.80	"	"	25.60
TR-18	67.52	14.68	"	"	17.52
SH-1	46.00	17.44	"	"	35.56
SH-3	66.60	13.67	0.03	"	19.63
SH-4	45.44	19.12	Negligible	"	35.44
J-4	19.40	4.50	0.50	"	76.00
J-32	63.76	14.48	0.70	"	19.06
J-44	33.56	8.42	2.00	"	56.01
J-45	59.60	6.70	Negligible	"	33.31

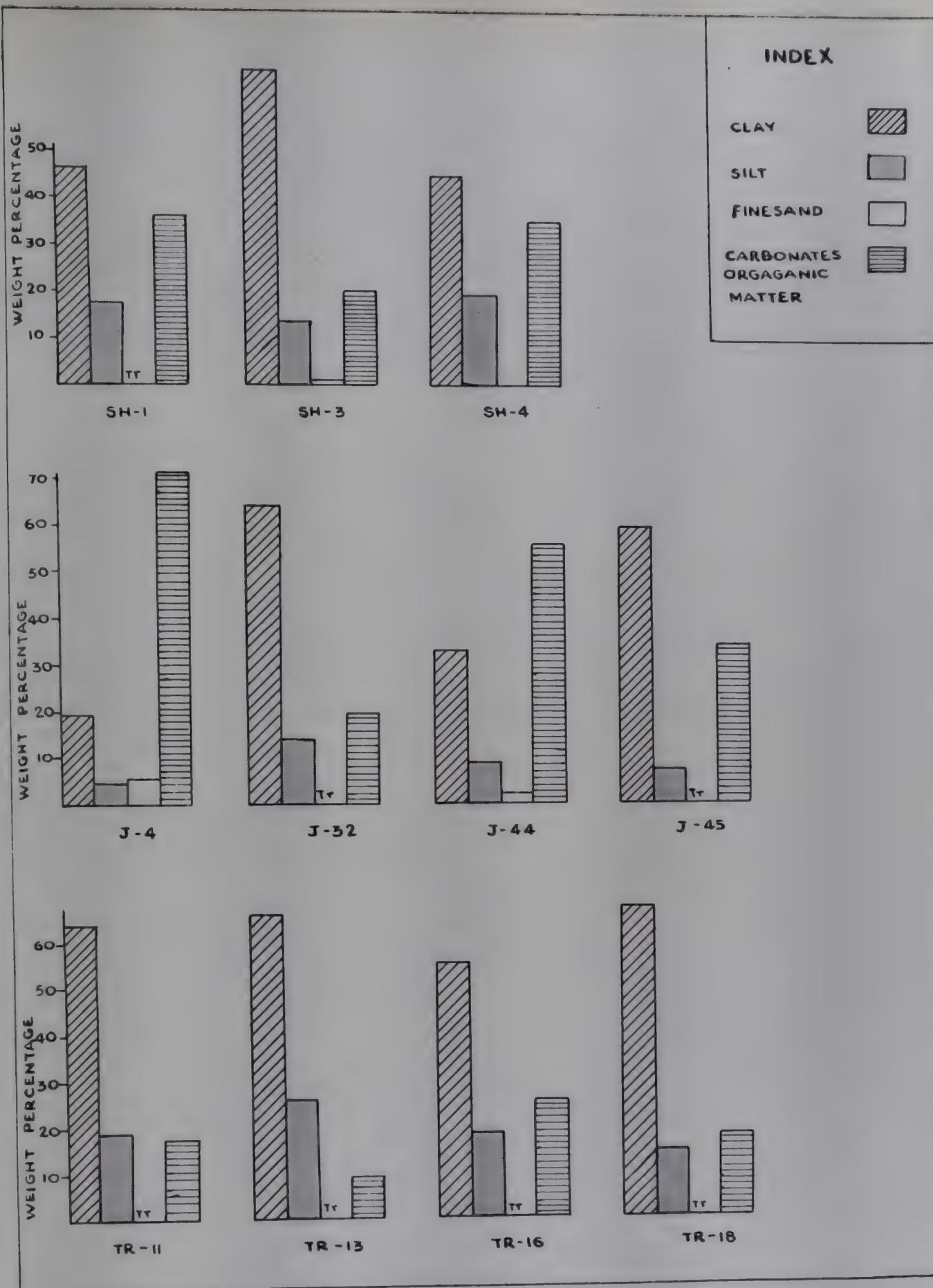


Fig. 2—Mechanical Composition of the Sediments

constituent. It may be mentioned here that the amount of samples received was found inadequate for heavy mineral analysis. However, a few grains of the heavies could be separated which include opaques, zircon, garnet and pyroxenes. The clay, carbonate and phosphate fractions have been dealt with separately.

Carbonates

Foraminifera and mollusks are the chief contributors of the sand-sized carbonates. Bryozoans and echinoidal fragments (Plate III, 38, 39, 40, 41) also contribute to some extent to this fraction. In the fraction coarser than sand, mollusks alone become the dominant constituents. The mollusks are highly fragmental in nature,



Fig. 4—*Globigerina bulloides*.

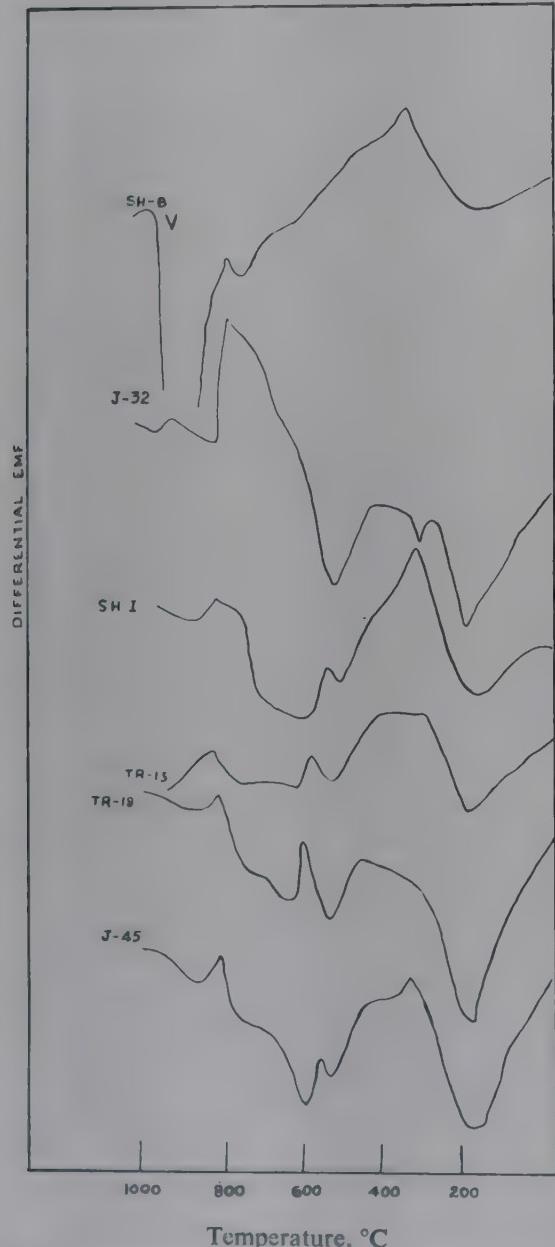


Fig. 3—Differential Thermograms of Dried Samples

without any appreciable wear. The distribution of foraminifera appears to be somewhat irregular in nature. While they are occurring abundantly in most of the samples collected from the J-group of stations, they are totally absent in the samples from the TR-group. Similarly the mollusks are also absent in the samples belonging to the latter group. This feature points, beyond any doubt, to the existence of two distinct marine provinces: in one, the relics of marine fauna are found in abundance, while in the other, they are totally absent. Aragonite forms the predominant inorganic constituent of the coarse fractions of some of the samples belonging to the J-series.

Organic Constituents; The foraminiferal assemblage noticed in the J and SH-group of samples is characterized by the occurrence of several genera, though only a few genera constitute the bulk of this population.

The genera that constitute the major assemblage in the J and SH-group of stations are: *Triloculina*, *Quinqueloculina*, *Spiroloculina*, *Globorotalia*, *Globigerina bulloides*, *Ammonia*, *Elphidium* and *Operculina*. The following are a systematic description of the foraminifera that were identified by their characters.

ORDER FORAMINIFERA d' Orbigny 1826.

FAMILY Miliolidae Ehrenburg 1839.

SUB FAMILY QUINQUELOCULINA Cushman 1917.

GENUS TRILOCULINA d' Orbigny 1926.

TRILOCULINA SP. [Plate I (1)]; Test elliptical; periphery carinated; 3 tube-shaped chambers arranged in three planes at angles of 120°; wall calcareous, imperforate; aperture terminal, semi-elliptical with a tooth-like projection; surface ornamented with curved ridges.

TRILOCULINA SP. [Plate I, (2); $\times 60$]; Test semi-globular; periphery smooth; wall calcareous, imper-

forate; aperture circular, toothed; surface ornamented with prominent longitudinal ridges.

TRILOCULINA SP. [Plate I (7); $\times 60$]—Test globular; chambers arranged in three planes at angles of 120° ; wall calcareous, imperforate; aperture circular with a short tooth-like projection; surface ornamented with broad and curved ridges.

TRILOCULINA SP. [Plate (8); $\times 70$]—Test short elliptical; wall calcareous, imperforate; aperture circular; surface ornamented with short and tough spines.

TRILOCULINA SP. [Plate I (9 & 10); $\times 60$]—Test spindle-shaped; 3 tube-shaped chambers arranged in three planes at angles of 120° ; terminal portion of the last chamber is slightly curved with a neck-like protrusion; aperture terminal and circular; surface smooth.

TRILOCULINA SP. [Plate I (11); $\times 80$]—Periphery smooth with chambers each one half coil in length; aperture terminal, semicircular with typical bifid tooth.

GENUS QUINQUELOCULINA d' Orbigny.

QUINQUELOCULINA SP. [Plate I (3 & 4); $\times 60$]—Test boat-shaped; periphery smooth; chambers coiled around an elongated axis in five different planes, chambers half coiled in length, three chambers visible from exterior of one side of test and four visible from the other side, aperture terminal, rounded with a simple tooth.

QUINQUELOCULINA SP. [Plate I (5); $\times 45$]—Test spindle-shaped; periphery smooth; chambers tube-shaped and half coiled in length, three chambers visible from exterior of one side of the test and four visible from the other side; wall calcareous, imperforate; surface smooth; the terminal position of the last chamber protruded into a neck, aperture terminal, large and circular.

QUINQUELOCULINA SP. [Plate I (6); $\times 60$]—Test spindle shaped; periphery carinated; wall calcareous; surface ornamented with slightly curved ridges; last chamber protruded into a neck; aperture terminal small and circular with a tooth.

FAMILY NUBECULARIIDAE JONES 1875

SUB FAMILY SPIROLOCULINAE Weisner 1920.

GENUS SPIROLOCULINA d' Orbigny.

SPIROLOCULINA SP. [Plate I (12); $\times 60$]—Test fusiform in outline with flat edge, chambers being added 2 to whorl on alternate sides and in single plane, sutures deeply depressed; wall calcareous, imperforate; aperture at the open end of the final chamber with a bifid tooth.

FAMILY GLOBIGERINIDAE Carpenter Parker and Jones 1862.

SUB FAMILY GLOBIGERININAE Carpenter Parker and Jones 1862.

GENUS GLOBIGERINA d' Orbigny 1826.

GLOBIGERINA SP. [Plate I (13, 14, 15) and plate IV; $\times 80$]—Test plano-convex; periphery lobed; chambers globular in shape, arranged trochospirally; sutures deeply depressed and distinct, curved; wall calcareous, coarsely perforate, cancellate surface; umbilicus large; aperture on the ventral surface, large, circular in outline, opening in the umbilicus.

SUBFAMILY ORBULINIDAE Schultz 1854.

GENUS ORBULINA d' Orbigny 1826.

ORBULINA SP. [Plate I (16); $\times 80$]—Test spherical, wall calcareous with perforations of various sizes.

FAMILY ROTALIDAE Ehrenberg 1839.

SUB FAMILY ROTALINAE Ehrenberg 1839.

GENUS AMMONIA Brunnich.

AMMONIA SP. [Plate III (34, & 35); $\times 70$]—Test biconvex; low trochospirally coiled of 3 or 4 volutions with sutures slightly curved, thickened, depressed on umbilical side; wall calcareous; irregular granules along umbilical fissures and plug in young forms which is broken up into numerous fused pillars and bosses in adult specimens as in Plates II & III (18, 22 & 33); in equatorial section rectangular chambers with height greater than length can be seen.

The forams at Fig. 17, 19, 20 and 21, plate II are also representatives of ammonia.

FAMILY CAMERINIDAE Bruguiere 1792.

SUB FAMILY CAMERININAE Bruguiere 1792.

GENUS OPERCULINA d' Orbigny 1826.

OPERCULINA SP. [Plate II (23 & 24); $\times 60$]—Test flat, bilaterally symmetrical, planispiral; periphery with thickened marginal cord; wall calcareous perforate, ornamented with bosses which are arranged in a regular fashion.

FAMILY GLOBOROTALIDAE Cushman 1927.

SUB FAMILY GLOBOROTALIA Cushman 1927.

GLOBOROTALIA SP. [Plate II (25 & 26); $\times 80$]—Shell lenticular, compressed, periphery lobed with a keel, chambers inflated, arranged in a low trochospiral coil; sutures distinct, curved. Slightly depressed; wall calcareous, coarsely perforate; umbilicus small; aperture on the ventral surface, elliptical in outline and placed near the umbilicus.

FAMILY ELPHIDIIDAE Galloway 1933.

SUB FAMILY ELPHIDINAE Galloway 1933.

GENUS ELPHIDIUM Montfort 1808.

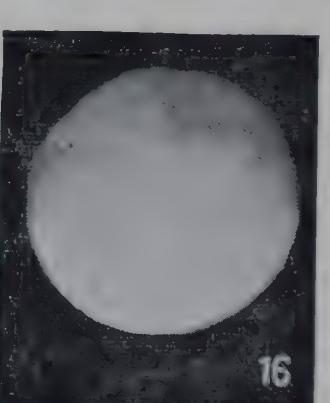
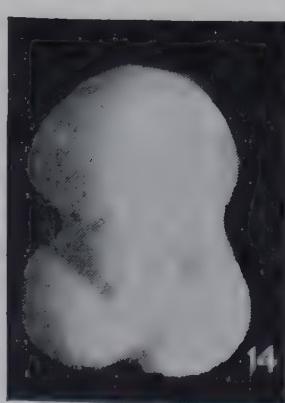
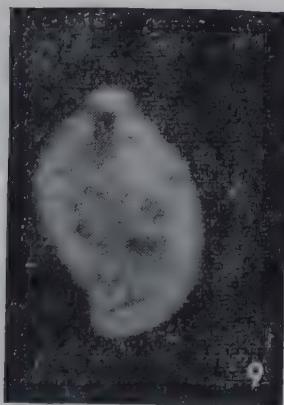
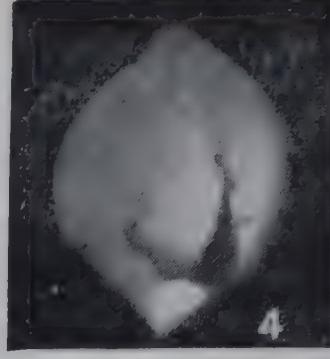


Plate I

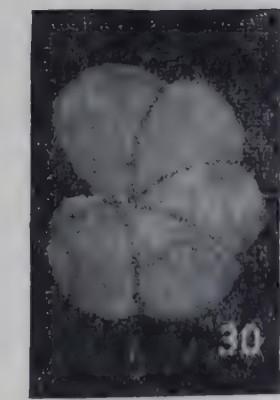
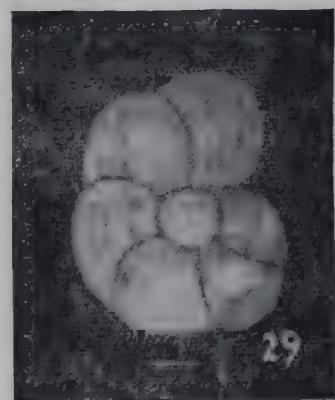
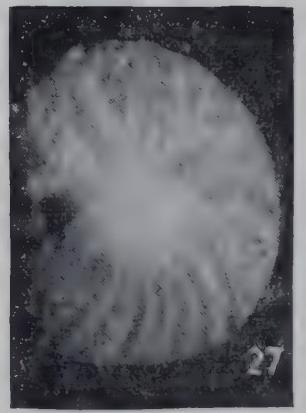
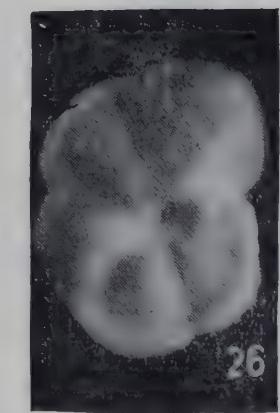
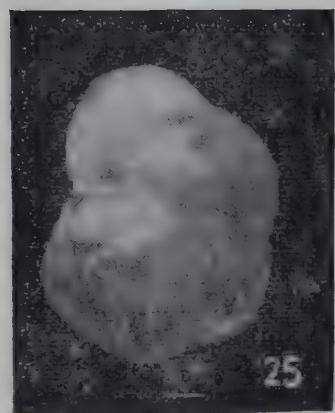
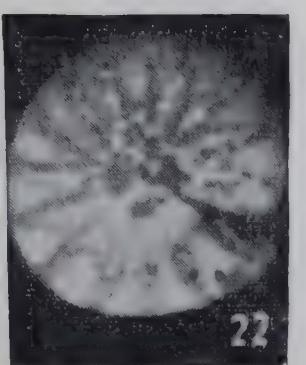
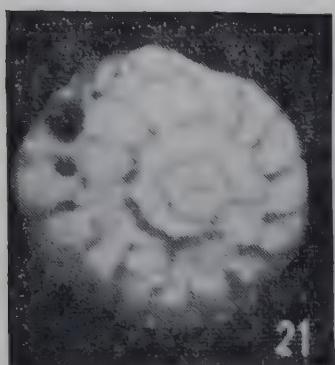
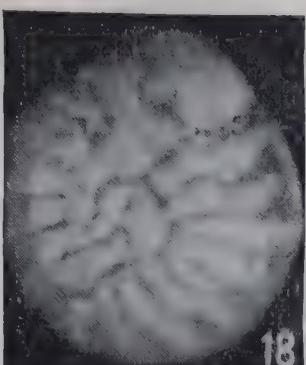


Plate II



33



34



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36



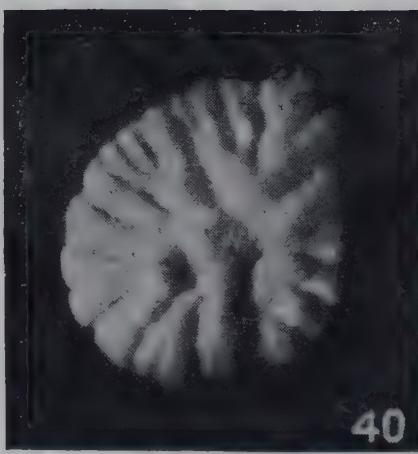
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38



39



40



41

Plate III

ELPHIDIUM [Plate II (27); $\times 60$]—Shell slightly biconvex, periphery smooth, chambers arranged in an involute planispiral coil; sutures distinct, slightly raised and curved; sickle shaped; wall calcareous, finely perforate; between adjacent sutures, triangular pits; surface with ridges paralleling periphery.

FAMILY NODOSARIDAE Ehrenberg 1838.

SUB FAMILY NODOSARINAE Ehrenberg 1838.

GENUS LENTICULINA Lamarck 1804.

LENTICULINA [Plate III (36); $\times 80$; Camera Lucida Trace]—Test trochospirally coiled, lenticular, periphery with keel; chambers increasing gradually in size and in general of greater breadth than height; sutures radial, elevated and straight, aperture radial at peripheral angle.

GENUS NODOSARIA Lamarck 1812.

NODOSARIA [Plate II (32); $\times 60$]—Test Multilocular, rectilinear; sutures distinct, perpendicular to axis of test; surface striate; aperture terminal, central and produced on a neck.

FAMILY CIBICIDIDAE Cushman 1927.

SUB FAMILY CIBICIDINAE Cushman 1927.

GENUS CIBICIDES de Montfort 1808.

CIBICIDES SP. [Plate II (29 & 30); $\times 60$ Camera Lucida Trace]—Shell biconvex, periphery smooth, dorsal more convex than ventral, chambers arranged in low trochospiral coil; sutures distinct in the ventral surface, deep wide and nearly flush with surface in the dorsal side; wall calcareous; coarsely perforate in the last whorl; aperture peripheral, extending on the ventral side with a typical slit-like extension between the last chamber and the preceding coil on the dorsal side.

FAMILY TEXTULARIDAE Ehrenberg 1838.

SUB FAMILY TEXTULARINAE Ehrenberg 1838.

GENUS TEXTULARIA Ehrenberg 1838.

TEXTULARIA SP. [Plate II (31)]—Test elongate, slightly wedge-shaped, compressed; periphery lobed, chambers inflated, slightly elliptical in shape, arranged biserially, two rows of chambers joined by a zig zag line; shell arenaceous; sutures depressed, clear, curved; aperture single and arch shaped at the base of the last chamber.

FAMILY NONIONIDAE Schultz 1854.

SUB FAMILY NONIONINAE Schultz 1854.

GENUS NONIONELLINA Voloshinova 1858.

NONIONELLINA [Plate III (37); $\times 60$]—Test biconvex; periphery smooth and slightly lobed; chambers arranged trochospirally in early coiling, later becoming planispiral and involute, chambers enlarging rapidly around

deep umbilicus; wall calcareous, finely perforate; aperture slit-like, at the base of the apertural face.

The forum at Fig. 28 could not be identified.

Inorganic Constituents: In samples J-4, J-5 and J-43, aragonite forms an important constituent (Fig. 5). They range in size from 0.5 mm to 1.0 mm and show extreme variation in shape: spherical, ovoid, elliptical, and sometimes cylindrical. Occasionally they occur in aggregation, the individual grains being bonded by calcareous mud. They also show variation of colour shades from white, creamy white, greyish brown and dark grey with surface usually smooth but occasionally pitted. In thin section they show a faint concentric rim around nuclei of quartz. X-ray studies of these colites, using Cu-K α radiation, confirmed that they consisted predominantly of aragonite with little quartz. It may be interesting to note that the occurrence of Argonite is restricted to the samples farthest from shore.

Clay Minerals

The clay minerals which constituted the finest fraction of the calcareous mud samples were separated by the previous method, and subsequently dried. The mineralogy of the clay fraction was interpreted primarily from data of x-ray diffraction and differential thermal analyses.



Fig. 5—Aragonite showing various shapes.

X-ray diffraction patterns were obtained in a Debye-Scherrer Camera of 114.6 mm diameter and also in a Guinier Camera. Filtered Cu-K α radiation was employed with x-ray tube running at 40 KV and 20 MA, and exposures of 7-9 hours for D. S. Camera and 4-5 hours for Guinier Camera. These data are given in the Table 3.

TABLE 3—X-RAY DATA OF THE CLAY FRACTION

Sample	Phase Identified		Remarks
	Major	Minor	
TR11	Illite	Quartz	1. One very weak line at 7.15° remains unassigned which is the strongest line of Kaolinite.
TR16	"	"	
TR18	"	" + Calcite traces	2. All the samples give high background scattering.
SH1	"	"	
SH4	"	"	
J-32	"	" + Calcite	
J-45	"	" traces	

DTA investigation of the samples was performed by a Linseis type fully automatic apparatus in the temperature range 26-1000°C, using a Pt/Pt-Rh thermocouple. Sample holder was made out of a thin platinum sheet. The reference substance used was ignited aluminium oxide and the rate of rise of temperature was kept at 10°C/min. D.T.A. diagrams of the oven dried samples are shown in Fig. 4 and the phases identified are presented in Table 4. Except one sample, (SH-3), all are clayey in nature and consist of illite and chlorite predominantly.

Identification of chlorites by x-ray data alone offers serious difficulties as the (001) spacing of kaolinite, 7.15 Å, interferes with (002) spacing of chlorites, 7.0-7.2 Å so that the kaolinite reflections overlap the even order chlorite reflections. This is specially true for the lower order diffraction and with these minerals present as minor constituents only, any assignment becomes unreliable. In differential thermograms, however, although both the minerals give endothermic peaks around 600°C, but their exothermic peaks are resolved; for kaolinite it appears at about 980°C and for chlorite, at about 800-850°C. In the present case therefore the very conspicuous exothermic peak at 780-830°C in all the cases, confirms chlorite unequivocally.

Phosphates

Estimation of phosphate-content was carried out by colorimetric method for 13 grab samples collected

from the three groups of Stations. The results are presented in Table 5. It will be seen that the phosphate-content of the sediments varies from 0.18 to 0.36 per cent whose distribution on the area has been presented in Fig. 1 No significant correlation was observed between these values with those of Nair¹ for dissolved phosphates. It may be recalled here that the chemical composition of Deccan trap shows that its P₂O₅ content

TABLE 4—DTA DATA OF THE CLAY FRACTIONS

Sample	Nature & Temp. of the peak		Phase Identified
	No.	Endothermic Exothermic	
J-45	160 s 530 w 600 m	300 m 820 m	Illite and chlorite major phase; possibly marine organic matter may be present.
TR-18	160 s 530 m 600 m	820 m	Illite and chlorite major phase.
TR-13	160 s 530 m 600 m	830	-do-
SH-1	130 w 520 w 580 m	330 s 820 m	Illite and chlorite major phase. Possibly marine organic matter may be present.
J-32	180 w 320 w 520 w	780 s 920 w	Illite and chlorite major phase, may contain montmorillonite, goethite mineral present as minor phase.
SH-3	100 w bulge 580 w bulge 750 m 920 s	330	Mostly calcareous clay, mixed with small proportion of chlorite and possibly dolomite.

NOTE: s, m and w mean strong, medium and weak respectively.

TABLE 5—PHOSPHATE CONTENT OF THE SEDIMENTS

Sample No.	% P ₂ O ₅
TR-6	0.1857
TR-10	0.1857
TR-13	0.1857
TR-14	0.1930
SH-1	0.2322
SH-3	0.2452
J-4	0.2692
J-5	0.2861
J-30	0.1843
J-32	0.3556
J-43	0.2778
J-44	0.2119
J-45	0.2249

averages at about 0.39 per cent and nowhere any higher value has been reported so far.

Discussions

From an overall study of the shelf sediments certain interesting features could be noticed. The sediments of the entire region, in general, represent calcareous muds containing various assemblages of fauna, viz. foraminifera (miliolides and rotalides dominant), mollusks, bryozoans and echinoidal fragments. The sediments belonging to the TR-group of stations, however, reflect a sharp contrast from this. The distribution of marine fauna is related to several environmental conditions but there are no such sharp deviations known for the locality of the TR-group.

In the carbonate fraction the proportion of aragonite tends to increase in the samples from the stations farther away from the shore and has its highest value at the station J-4. Phosphate-content of the sediments also shows a slight but significant increase in its value in the sample from such stations. These data therefore indicate that the marine environment tends to favour inorganic precipitation only in regions situated away from the shore.

The nature of the sediments of the region investigated, in general, suggests depositional characteristics. These environments are usually unfavourable⁵ for phosphoria formation, for, any phosphate formation, if occurring in areas of high sedimentation rates, would be covered by fine sediments and large scale formation would be prevented. In non-depositional environments, however, where the ocean bottom currents are concentrated and which may exist along certain tectonic features like off-shore banks, escarpments, walls of submarine canyons etc, under favourable conditions, any fine sediments that reach the bottom are soon washed away and the slow accretion of electrically charged colloidal precipitates of phosphate may take place unimpeded by clastic sedimentation. All of the localities where undersea phosphorites are found are therefore, essentially in non-depositional⁶ environments.

The results¹ of the Angria Bank expedition reveal very high values of dissolved inorganic phosphates off Ratnagiri. Their values (as P_2O_5) were of the order of 2-3 $\mu g.$ atom/l, upto a depth of 30 metres, below which they were higher than 4 $\mu g.$ atom/l. In some of

the samples, at depths of 70 metres or below, they rose to 12 $\mu g.$ atom/l. It is known that the dissolved phosphates of the Indian Ocean are, in general, higher than those of the Atlantic and somewhat less than those of the Pacific, but range around 0.3 $\mu g.$ atom/l at depths of 100 metres and reaches its maximum value (3 $\mu g.$ atom/l) at about 1000 metres. The higher values obtained around the Western Coast therefore, may suggest² restricted circulation or drainage from the Indian subcontinent. In the absence of detailed data about the sea floor topography available to present authors, no specific conclusion could be drawn about the circulation effects. However, drainage from the Deccan trap is not very likely to be the predominant source for undersea phosphoria formation in the region. The present investigations on the sediments were too meagre to permit drawing definite inferences. However, the data do suggest that the economic formation of phosphorites are unlikely to be found in the region covered by the cruises. But the increased non-depositional characters beyond the area require fresh investigation from this point of view. It looks advisable, therefore, to extend these studies on samples obtainable from zones beyond the covered area.

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Behaviour of a Soluble Phosphatic Fertilizer With Some Indian Soils

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Different soils have different phosphate-fixing capacities, the latter depending upon the nature and amount of clay minerals, calcium carbonate and active phases of iron and aluminium present. The illite type fixes more phosphate than the montmorillonitic type of clay mineral. A dose of 20 mg. P_2O_5 /100 g. soil in case of Allahabad, I.A.R.I. and Ludhiana soils is optimum at which the soil pyosphate and solution phosphate remain in equilibrium. Soils containing calcium carbonate release some phosphate after 12 hours' contact when applied at higher doses, the release being maximum in soils containing high calcium carbonate. It is possibly due to the initial adsorption of phosphate on the surface of calcium carbonate and subsequent release of the adsorbed phosphorus that precipitation of iron, aluminium and calcium bound phosphates finally occurs.

When soluble phosphatic fertilizers are added to the soil, phosphorous fixation takes place by one or more of the three mechanisms, viz. (1) adsorption, (2) isomorphous replacement, and (3) double decomposition. These processes generally reduce the efficiency of applied phosphatic fertilizers to between 1 and 20 per cent. The fixation of phosphate depends on the nature and amount of iron, aluminium, calcium and clay present in the soil. Ghosh and Bhattacharya¹ have found that soluble phosphates formed insoluble compounds with almost all inorganic constituents of the soil.

Several attempts have been made to assess the extent of fixation when soluble phosphates are applied to soil²⁻⁸, and also to determine the chemical reactions involved⁴⁻⁸. It was shown that most of the soluble phosphates formed insoluble iron and aluminium phosphates regardless of pH.

Because of the complex nature of the reactions involved, phosphate-fixing power of some Indian soil was studied in relation to their clay minerals, free calcium carbonate and iron oxide contents. The effect on such fixation of varying doses of phosphate application with the time of contact with the soils was also investigated.

Experimental

The clay fractions of the soils were separated by the international method⁹. They were converted into H-clays in the usual way, oven-dried and the lumps formed were powdered in an agate mortar and passed through 100 mesh (B.S.S.) before use for fixation studies. The soil samples studied were: (1) Allahabad Sandy loam, (2) Amroati black loam, (3) Ludhiana sandy clay loam, (4) I.A.R.I., New Delhi, sandy clay loam, and (5) Sindri red sandy clay loam (Tables 1 & 2).

The phosphatic fertilizer was added to the soil in the following way: 10 g. of soil were taken in a conical flask to which monocalcium phosphate (major constituent of superphosphate) solution was added at the rate of 5, 10, 20 and 30 mg. of P_2O_5 per 100 g. The flasks were shaken vigorously and filtered at the end of 0, 6, 12 and 24 hours. The P_2O_5 content in the filtrate was determined volumetrically as ammonium phosphomolybdate¹⁰. A similar set of experiments was also done with the clay fractions. For this purpose, 1 g. of clay fraction was treated with monocalcium phosphate solution, at the rate of 30 mg. P_2O_5 /100 g. of clay. They were shaken vigorously and centrifuged after 0, 12 and 24 hours. The P_2O_5 in the centrifugate was estimated colorimetrically, because of its low concentration, by

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TABLE 1—PHYSICO-CHEMICAL PROPERTIES OF VARIOUS SOIL TYPES

Sl. No.	Soil Type	Clay Minerals Present	Sand %	Silt %	Clay %	Total Al_2O_3 %	Total Fe_2O_3 %	Total free Iron as Fe_2O_3 %	Total free CaCO_3 %	Loss on Ignition %	pH	C.E.C. m.e./ 100 g.
1. Allahabad Sandy Loam	Illite mainly, Kaolinite & Montmorillonite are also present. Hydrates of alumina may be present in small amount		80	7	7	3.19	3.47	0.30	4.0	5.13	8.2	3.4
2. Amroati Black Loam	Montmorillonite. mainly Kaolinite may be present in small amount		31	22	27	11.61	9.28	0.60	10.0	10.22	8.3	52.9
3. Ludhiana Sandy Clay Loam	Illite mainly. Kaolinite & Montmorillonite are also present		70	9	16	3.95	3.04	0.61	1.5	3.69	8.45	8.2
4. I.A.R.I. New Delhi Sandy Clay Loam	Illite mainly. Montmorillonite & Kaolinite are also present		61	8	16	3.48	2.62	0.45	4.0	3.28	7.7	10.6
5. Sindri Red Sandy Clay Loam	Illite mainly. Kaolinite & Montmorillonite are also present		58	5	29	7.11	5.27	1.19	—	5.07	6.65	12.6

TABLE 2—CHEMICAL COMPOSITION OF SOIL CLAYS, %

Sl. No.	Soil Clay Type	Total Al_2O_3	Total Fe_2O_3
1. Allahabad sandy loam	8.0	20.4	
2. Amroati black loam	21.9	15.7	
3. Ludhiana sandy clay loam	14.3	23.8	
4. I.A.R.I. New Delhi sandy clay loam	18.3	17.2	
5. Sindri red sandy clay loam	23.5	16.7	

TABLE 3—PHOSPHATE FIXATION BY SOIL CLAYS

Sl. No.	Soil Clays	Time of Contact, 24 Hours			Total Free Iron in Clays as Fe_2O_3 , %
		% of Added P_2O_5	% of Added P_2O_5	% Decrease in P_2O_5 due to Fixation	
1. Allahabad Clay	84.7	68.6	16.1	4.2	
2. Amroati Clay	58.6	25.0	33.6	2.1	
3. Ludhiana Clay	50.9	35.4	15.5	7.3	
4. I.A.R.I. Clay	57.1	36.0	21.1	3.7	
5. Sindri Red Clay	81.6	50.0	31.6	2.9	

TABLE 4—VARIOUS FORMS OF PHOSPHATES IN SOILS
(untreated)

Sl. No.	Soil Types	Total HC1- Soluble, P_2O_5 %	Total Al-P, ppm	Total Fe-P, ppm	Total Ca-P, ppm
1. Allahabad Sandy Loam	0.16	—	—	—	—
2. Amroati Black Loam	0.13	10	8	420	
3. Ludhiana Sandy Clay Loam	0.13	13	32	220	
4. I.A.R.I. New Delhi Sandy Clay Loam	0.10	Trace	35	175	
5. Sindri Red Sandy Clay Loam	0.07	„	29	24	

chlorostannous-reduced molybdophosphoric acid blue method in hydrochloric acid¹¹.

The free iron oxide was analysed in the soils and clays (Table 3) by the buffered sodium dithionite extraction method¹². The oxide-free clays were treated exactly as above with monocalcium phosphate solution and phosphate fixation was determined in the same way.

Aluminium, iron and calcium-bound phosphates in the original soil were estimated (Table 4) according to the method of Chang and Jackson¹³.

Results and Discussion

From the nature of fixation of phosphates by the soil (Figs. 1-5), the following important points emerge.

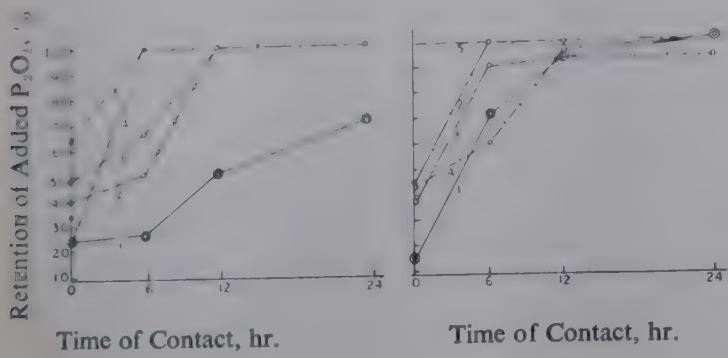


Fig. 1
Dose: 5 mg P_2O_5 /100 g. Soil

Fig. 2
Dose: 10 mg. P_2O_5 /100 g. Soil

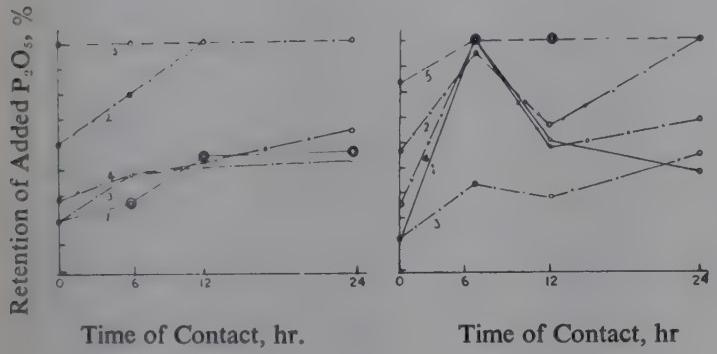


Fig. 3
Dose: 20 mg. P_2O_5 /100 g. Soil

Fig. 4
Dose: 30 mg. P_2O_5 /100 g. Soil

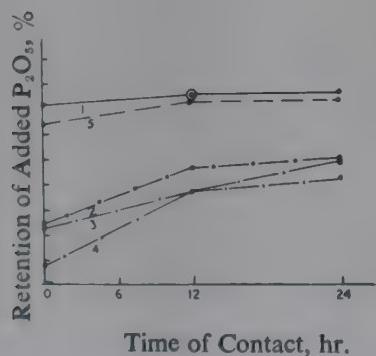


Fig. 5
Dose: 30 mg. P_2O_5 /100 g. Soil Clay

Figs. 1-5—Phosphate Fixation by Various Soils and Soil Clays

- Legend: 1. Allahabad Soil
2. Amraoti Soil
3. Ludhiana Soil
4. IARI Soil
5. Sindri Red Soil

The immediate fixation is generally small, but tends to maximize after 6 to 12 hours' reaction; this is particularly true with doses 5 to 20 mg. With 30 mg. the maximum fixation occurs in about 6 hours. In contrast to the other doses, the fixation corresponding to this dose is reversed after 12 hours' reaction. After 12 hours upto 24 hours the fixation remains more or less unaltered.

Although the rate of fixation of phosphate by different soils is of a similar nature, a closer scrutiny reveals certain significant differences amongst the soils.

Sindri soil is characterized by nearly 100 per cent fixation taking place almost immediately, for all the doses employed. Fixation is usually low for the Allahabad soil and to a certain extent for the I.A.R.I. and Ludhiana soils. The markedly low fixation with 20 mg. and the reduction mentioned above of the reversal of fixation at 30 mg. dose are particularly noticeable.

All the soils contain small amounts of free iron oxide, the maximum being present in the Sindri red soil, which is acidic in reaction, the rest contain varying amounts (1.5 to 10 per cent) of calcium carbonate and their pH values are also in the alkaline range (7.7 to 8.5). Of the different forms of phosphorus the maximum amount is indeed constituted of calcium-bound phosphorus (Table 4), followed by iron-phosphorus. This is explained by the presence of free iron oxide and calcium-carbonate in the soils and their high pH values.

The rates of phosphate fixation by clays isolated from the soils are entirely of a different nature, as can be seen from a comparison of the Figs. 1-4 with Fig. 5. The behaviour of Allahabad soil and its clay fraction may be cited as an instance in point. While the soil fixes phosphate slowly and never so high except with 30 and 10 mg. doses, the clay fraction becomes the highest and quickest fixer of phosphate. This is followed by the Sindri clay, but the corresponding soil is a very quick and 100 per cent phosphate-fixer. Again by comparison, the Amraoti clay has a much lower phosphate-fixing capacity than the soil itself. The I.A.R.I. and Ludhiana clays have similarly a low phosphate-fixing capacity.

If the comparison of the soils and the clays is restricted to the 30 mg. dose only (Figs. 4 and 5), the change in the pattern of phosphate fixation is much more noticeable. The sudden rise in fixation observed in the case of soils is completely absent in clays, which have a very slow and smooth rate of fixation.

From Table 3, it is obvious that after the removal of free iron oxide from soil clays, Allahabad clay is the

highest fixer of phosphate; followed by Sindri red, I.A.R.I. and Ludhiana clays; Amroati clay is the lowest fixer of phosphate. By referring to nature of the clay minerals (Table 1), it is noticed that the illitic clays fix more phosphate than the montmorillonite clays. Comparing the soil clays having similar type of clay mineral's, the variation in phosphate fixation is due to the presence of minerals in minor phase. The highest fixation with Allahabad clay may be also due to the presence of hydrates of alumina.

The reduction in phosphate fixation by clays after the removal of free iron oxide by the dithionite extraction shows the part played by the latter. But the amount of reduction is not proportional to the contents of free iron oxide (Table 3) showing that the oxides present in different clays are not equally active in phosphate fixation.

The initial high fixation of phosphate by almost all soils is done mostly by the clays present in them. The variation in fixation may be due to the variation in the amount and type of clay minerals, free iron, aluminium and calcium carbonate present in the soil. Sindri red and Amroati soils contain the highest amount of clay, free iron oxide and other minerals (Table 1), which may account for their highest fixation throughout the varying doses and time of contact.

At 20 mg. dose, the lesser variation in phosphate fixation in case of Allahabad, I.A.R.I. and Ludhiana clays may be due to the equilibrium achieved between soil phosphate and solution phosphate which thus indicates the optimum point of the different doses.

At 30 mg. dose, the reversal of phosphate fixation by soils containing varying amounts of calcium carbonate (1.5 to 10 per cent) after 12 hours' contact shows the effect of the latter on such a process. Soils, having the highest calcium carbonate release maximum

with respect to those containing low amount of the latter. Mattingly¹⁴ observed that phosphate ions are absorbed on the surface of calcium carbonate at a low concentration and precipitates as calcium, iron and aluminium phosphates, when P_2O_5 is applied at the higher dose. On the basis of this conclusion, the release of P_2O_5 after 12 hours' contact is probably due to its release from calcium carbonate and subsequent precipitation as iron, aluminium, calcium and clay-bound phosphates, thus showing increased fixation after 24 hours' contact.

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Interphase Chromosome Volume-Radiosensitivity Relationship in Some Diploid Annuals*

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Eleven diploid annuals were investigated in the Gamma Field of the Bhabha Atomic Research Centre, Trombay, with lethality and growth inhibition as the criteria of radiation damage. Growth inhibition was determined at two levels, i.e., severe (85 per cent, reduction) and slight (15-20 per cent reduction). Growing plants were chronically irradiated approximately 10 hours a day for 8-12 weeks, from seedling stage to maturity. The dose rate required to induce a desired effect was taken as a measure of radiosensitivity. For equivalent effects in different species, the dose rates showed negative correlations with nuclear volumes (e.g. -0.664 between nuclear volume and lethality). The correlations were better with interphase chromosome volumes (ICV): -0.720 between ICV and lethality, -0.729 between ICV and severe growth inhibition, and -0.779 between ICV and slight growth inhibition.

These observations confirm Sparrow's suggestion regarding the possibility that the radiosensitivity of other plant species can be predicated if their ICV values are known.

In studying the radiosensitivity of plants with respect to lethality and growth inhibition, the cell nucleus is generally considered to be the principal site of radiation damage. It is mainly due to the work of Sparrow and his coworkers⁴⁻⁷ that a direct correlation between radiosensitivity and nuclear volume or better interphase chromosome volume (ICV) has been established for a number of plant species. The present report provides additional information in support of the correlation.

Materials and Methods

Altogether eleven herbaceous dicotyledons belonging to six families were used. While six of them were local cultivated varieties, the remaining five were wild species collected from Trombay.

Potted plants were irradiated chronically at the Gamma Field, (480 Curie Co⁶⁰ source of the Bhabha Atomic Research Centre, Trombay) for 6 to 32 weeks

depending upon the maturity of each species. At the beginning of exposure the plants were at four-leaf stage. While *Lens*, *Chrysanthemum*, *Phaseolus* and *Cicer* were irradiated during October-January, the remaining species were irradiated during April-September of the following year. *Cajanus* plants were irradiated over extended period of 32 weeks including both winter and summer months. Temperature, rainfall and humidity fluctuations during the period of experiment are given in Table 1.

The plants were arranged in isodose arcs around the gamma source at distances varying from 4.75' to 36.00'. The dose rates at the nearest and the farthest distances were 211 R/hr. and 4.6 R/hr. respectively. Fricke dosimeters were used for the measurements of doses from 1000 R to 40,000 R, while thermoluminescent dosimeters were used from 10 mR to 10,000 R. The dose measurements were taken at the middle of the total irradiation period of a particular species. Moreover, as the height of a plant during its growth changed resulting in a variation in diagonal distance of the growing point from the source, the dose rates were recorded at the middle height of the plants. The number of plants per exposure were 10 to 12 and the number of exposure

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TABLE 1—AVERAGE TEMPERATURE, RAINFALL AND HUMIDITY DURING THE PERIOD OF EXPERIMENT

Month	Temperature, °C			Humidity, %	Rainfall, mm
	Maximum	Minimum	Average		
May, 1966	32.9	26.7	29.5	67	9.4
June, 1966	31.4	26.9	29.0	77	192.7
July, 1966	29.8	26.0	27.7	83	944.0
August, 1966	29.6	25.5	27.3	81	122.6
September 1966	30.9	25.0	26.9	85	354.5
October 1966	30.7	24.7	28.0	68	11.4
November 1966	33.6	22.9	27.5	59	5.5
December 1966	31.8	19.4	24.7	58	0.0
January 1967	30.5	16.8	22.9	51	0.0
February 1967	33.5	18.7	25.3	55	0.0
March 1967	31.9	22.5	26.8	64	0.0
April 1967	32.7	26.1	29.0	72	0.0

for a species varied from 8 to 12. On an average the plants were exposed daily for 10 hours.

Lethality and growth inhibition were the two criteria used to measure the radiosensitivity. Growth inhibition was determined at two levels, namely severe (85 per cent reduction) and slight (15-20 per cent reduction). Data on height, number of leaves, number of branches and dry weight were recorded at the initiation of maturity of the control plants and the end points, severe and slight growth inhibition, were determined from the exposure-growth curves. In the case of *Cajanus*, *Amaranthus* and *Sesbania* these end points were approximate since sufficient numbers of exposures were not available to draw the growth curves.

For histological data, primary vegetative meristems from seedlings at four leaf stage were evacuated and

fixed in Randolph's Navashin for a minimum of 24 hours and embeded in paraffin wax through xylol-alcohol series. Staining was done in methyl violet and orange G. Ten nuclei from tunica and outer corpus of each of the two meristems of a species were measured and for each nucleus an average of two diameter measurements, one at right angle to the other, were taken for calculation of the nuclear volume by applying the formula of a sphere. Interphase chromosome volume was determined by dividing the nuclear volume by the somatic chromosome numbers.

Results

Many of the morphological abnormalities were specific, for instance, fasciation was observed in *Sesbania* and *Crotalaria*, and stem swelling in *Cajanus*. But puckering and mottling of young leaves were common in all the species. The time of initiation and severity of this symptom varied from species to species. When *Malachra*, *Corchorus*, *Crotalaria* and *Cajanus* plants were placed at the same time inside gamma field, *Crotalaria* showed puckering and mottling of leaves first of all followed by *Cajanus*, *Corchorus* and *Malachra*. Moreover, symptom was most severe in *Crotalaria* and least in *Malachra*. As will be seen in Table 2 radiosensitivity of these species are in the same order. Such qualitative comparison worked out well when the plants of different species were placed at the same time but it was difficult to compare two sets of plants placed at different times.

Data relating to chromosome number, nuclear volume and interphase chromosome volume and the chronic exposure required for lethality, severe and slight growth inhibitions in eleven annual herbs are presented in Table 2.

TABLE 2—CHROMOSOME NUMBER, NUCLEAR VOLUME, INTERPHASE CHROMOSOME VOLUME AND CHRONIC IRRADIATION TOLERANCE DATA OF 11 SPECIES OF ANNUAL HERBS

Species	Nuclear Volume, μ ³	Somatic Chromosome no.	Interphase Chromosome Volume	Lethal Exposure, R/hr	Exposures Producing Growth Inhibition, R/hr	
					Severe	Slight
1. <i>Nigella sativa</i>	599.2	12	49.9	16.6	12.0	2.0
2. <i>Chrysanthemum carinatum</i>	369.1	18	22.0	28.0	22.5	3.8
3. <i>Sesbania bispinosa</i>	195.4	12	16.3	59.0	42.0	9.0
4. <i>Lens esculenta</i>	202.7	14	14.5	45.5	25.0	4.0
5. <i>Crotalaria juncea</i>	147.5	16	9.2	78.0	58.0	5.0
6. <i>Cicer arietinum</i>	121.7	16	7.6	235.0	170.0	—
7. <i>Corchorus capsularis</i>	73.9	14	5.3	101.0	80.4	20.0
8. <i>Phaseolus aureus</i>	99.3	22	4.5	84.0	63.0	33.0
9. <i>Cajanus cajan</i>	96.1	22	4.4	42.0	26.0	8.9
10. <i>Amaranthus paniculatus</i>	254.5	64	3.9	—	144.0	47.0
11. <i>Malachra capitata</i>	137.5	56	2.4	110.0	85.0	28.0

Variation in the chromosome number among the species is small, the maximum being only about fivefold. Within such a variation, chromosome number alone seems to have little or no effect on radiosensitivity. For instance, *Sesbania bispinosa* and *Nigella sativa* have the same chromosome number but the sensitivity of the latter is four times higher than that of the former. This indicates that chromosome number alone cannot be treated as a criterion for determining radiosensitivity.

A variation in nuclear volume is accompanied by a corresponding significant variation in the daily exposure necessary to produce lethality (Table 3).

TABLE 3—TOTAL CORRELATION CO-EFFICIENT OF NUCLEAR VARIABLES AND RADIOSENSITIVITY END-POINTS

	Lethality	Severe growth Inhibition	Slight Growth Inhibition
Nuclear Volume	- 0.664*	- 0.531	- 0.576
Interphase chromosome volume	- 0.720*	- 0.729**	- 0.779**

*Significant at 5% level

** Significant at 1% level

Fig. 1 gives the regression line of nuclear volume versus lethality relationship. As regards growth inhibition, the relationship though apparent is not significant.

The absence of variation in sensitivity in relation to chromosome number needs reconsideration in view of the relationship existing between nuclear volume and sensitivity. Although species having exactly the same nuclear volume but different chromosome number are not included in the present experiment we can reasonably compare *Malachra capitata* ($137.5 \mu^3$ NV and 56 chromosomes) and *Crotalaria juncea* ($147.5 \mu^3$ NV and 16 chromosomes). The difference in nuclear volume is small but chromosome number of the former is three and half times of the latter. Daily dose rate for lethality in *Malachra capitata* was one and half times of the other. Hence, it may be noticed that additional chromosome increases the resistance when nuclear volumes are almost the same. In fact, chromosome number and nuclear volume behave as independent variables. That is illustrated by comparing the range of variation of nuclear volume and chromosome numbers in the first nine species in Table 2. For example, *Nigella sativa* and *Sesbania bispinosa* have the same chromosome number but about three fold difference in nuclear volume. Correlation between the interphase chromosome volume and the three radiosensitivity end points are significant (Table 3). This

indicates that chromosome number must be considered in evaluating nuclear volume as a factor determining radiosensitivity. Exposures required to produce comparable effect in each species were plotted against their ICV in Fig. 2 to 4. The regression lines for the end points were estimated by slopes -0.794, -0.897 and -1.012. While the slopes of the line relating to lethality and severe growth inhibition is less than -1, it is likely that it might be closer to -1 when more extensive data are available.

Points in Fig. 1 to 4 show a good amount of scattering around the regression line, *Cicer arietinum* shows exceptionally high resistance. *Cajanus cajan* was more sensitive than expected and incidentally this species received longest period of exposure (32 weeks).

Discussion

The species included in the present study differed in relation to their time for maturity. *Amaranthus paniculatus* took only 6 weeks while *Cajanus cajan* took 32 weeks to mature. It was necessary to find sensitivity difference, if any, in different phases of plant growth. At least in *Indigofera glandulosa* reproductive stage was more sensitive than vegetative stage (data not presented here). Hence, it was considered better to include all stages of growth upto maturity and treat the difference due to different periods of growth as their inherent difference.

The data presented show that interphase chromosome volume is an excellent index of radiosensitivity giving consistently better correlation than nuclear volume. The present experimentation avoided polyploid species and also those with high chromosome numbers. Though polyploid species were not used, correlation with nuclear volume did not improve and this suggests that, however, small may be the difference in chromosome number between species they should be accounted for and that can be explained by interphase chromosome volume. It will be seen in the present experiment that a few species like *Cajanus cajan* and *Cicer arietinum* show a large amount of deviation from the regression line. This seems to be due to other superimposed factors playing a modifying role (Sparrow⁴ and Yamashita⁸). That nuclear volume as well as interphase chromosome volume are important factors determining radiosensitivity differences observed between species is well known (Carpella and Conger¹, Gomez-Campo and Delgado², Osborne and Lunden³, Sparrow^{6,7}). It is now generally considered that nucleus is the major site of radiation injury in a wide variety of organisms (Wolff⁹). Therefore, it would seem logical to regard nucleus and its

Fig. 1

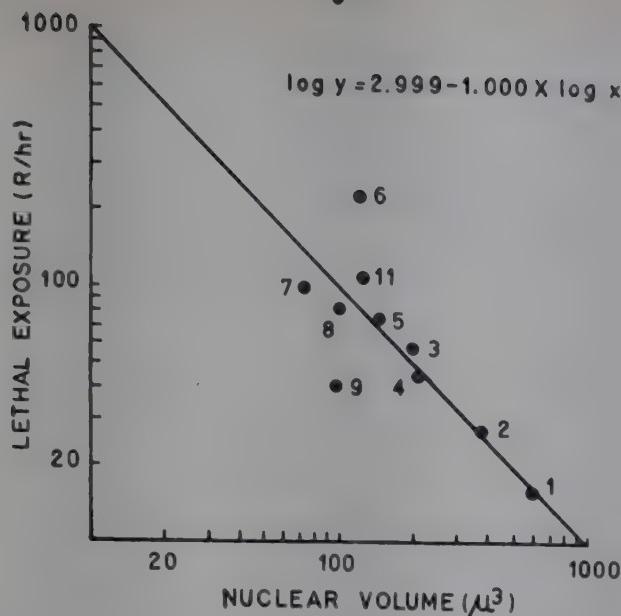


Fig. 2

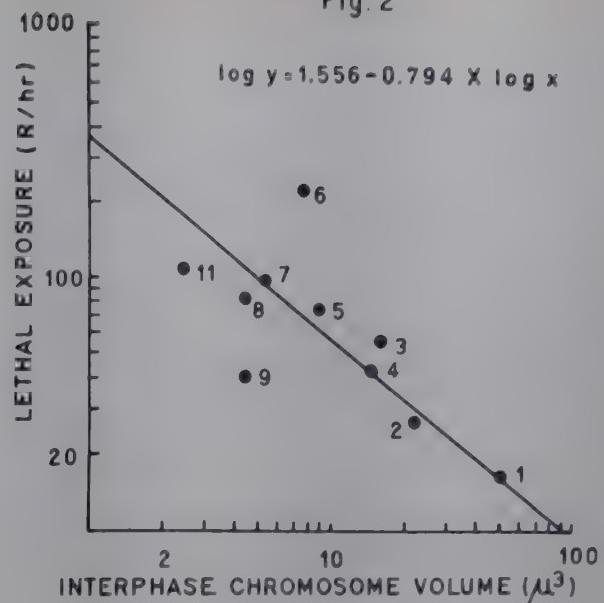


Fig. 3

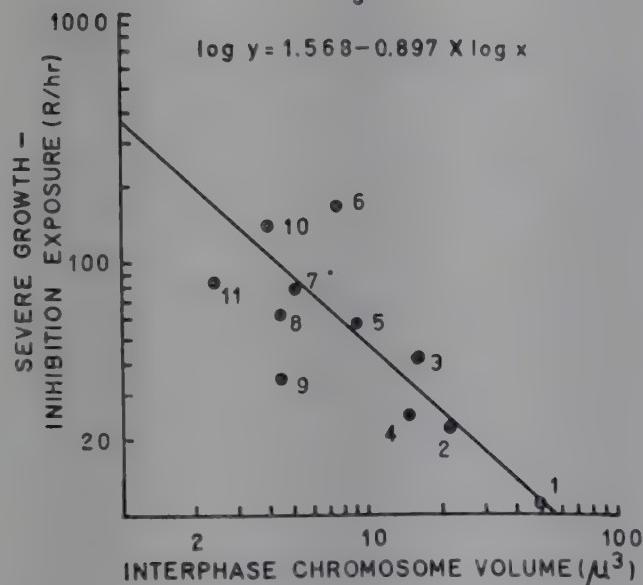


Fig. 4

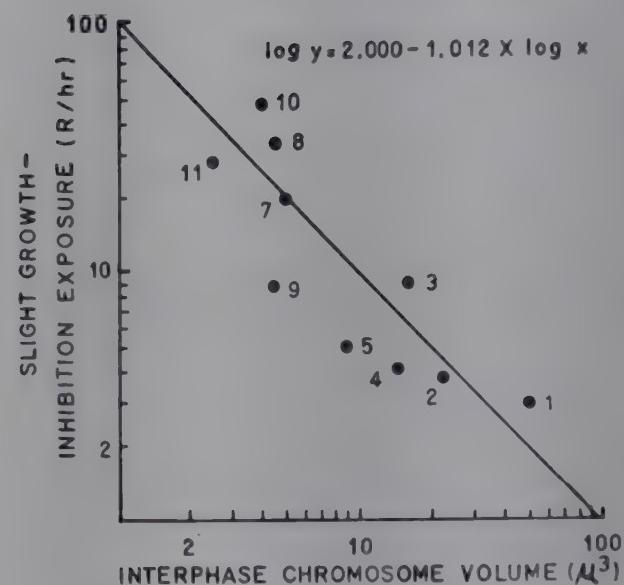


Fig. 1—Regression Line and Equation of Nuclear Volume with Exposures Required to Produce Lethality.

Figs. 2-4—Regression Lines and Equations of Interphase Chromosome Volume with Exposures Required to Produce Lethality and Growth Inhibition.

component chromosomes as the target and the interphase chromosome volume-sensitivity relationship confirmed here means to correlate differences in target volumes with differences in sensitivity.

Moreover, the slopes of the regression lines for these relationships are very near to -1 indicating that the quantum of energy absorbed per interphase chromosome is constant and independent of species variation.

Sparrow⁵ et al indicated that from this relationship prediction is possible within certain limits of error. Such prediction has got practical implication in radiobiology when dealing with plants the radiosensitivity of which has not been worked out. Dose rates producing standard effect can be directly read out from regression lines when nuclear volume and chromosome numbers are known.

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Temperature Coefficient of Kovats Retention Index As a New Parameter in the Identification of Gas Chromatographic Peaks*

By

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Linearity in the variation of retention indices with column temperature has been established as a general rule for non-polar solutes in all stationary liquids. In GLC this rule is probably valid for polar compounds also. The temperature coefficients of retention indices of hydrocarbons in non-polar liquids decrease in the order aromatic >cyclic>tetra alkyl paraffins>di- and mono-alkyl paraffins. Co-elution phenomenon has been studied for 40 hydrocarbons in SE-30 in the range of 80-225°C. Coelution among isomeric alkanes is quite common, but certain restrictions have been observed in the coelution of iso and cyclic paraffins. Among saturated hydrocarbons a cycloparaffin can co-elute with a large number of alkanes and by injecting a proper cycloalkane with unknown alkanes, the latter can be identified. Many co-elution compositions found from experimental I-T plots as well as from comparison with other stationary liquids have been listed. This information is considered very valuable in the proper interpretation of complex chromatograms. Vapour pressure fails to explain the co-elution phenomenon of even non-polar solutes in non-polar stationary liquids. A parameter derived from temperature coefficient of I-T plots and from carbon number of particular normal paraffins has been utilized in the subclassification of all hydrocarbons into types. Utilization of this parameter and the shift in co-elution temperature of a few selected hydrocarbons have been proposed as new methods of classification of stationary liquids. It has been suggested that retention indices should be reported in at least three temperatures for the sake of maximum information.

In recent years it has been established that retention index (I) provides the most suitable system to report retention data in analytical gas chromatography (GC). One great advantage of the retention index system is

that it readily brings to notice many and varied fine aspects of comparison and correlation between retention characteristics and structures of sample molecules. Utilization of this aspect together with information derived from the use of column temperature (T) in a new role in peak identification is the object of the present investigation. In programmed temperature GC column temperature has been given a different role. Several

*This paper was presented at the Gas Chromatography Symposium held during May 20-21, 1968 at the Indian Institute of Petroleum (CSIR) Dehra Dun.

workers¹⁻³ have made important observations on the dependency of retention index upon column temperature. Ette and Billeb⁴ observed a linear variation of I of hydrocarbons with column temperature in squalane (SQ). In the present work it is proposed to correlate the temperature co-efficient of I of hydrocarbons with their structural features with a view to developing new peak identification parameters and also to find out new methods of hydrocarbon type analysis.

Experimental

An Aerograph Hi-Fi model 600D gas chromatograph equipped with flame ionization detector was used in this work. The column was 20' \times 1/8" O.D. copper refrigeration tubing packed with 60-80 mesh (B.S.S.) acid washed silanized Chromosorb-W, coated with approximately 5 per cent SE-30** by the percolation technique, the carrier gas was nitrogen. The gas hold-up was determined from methane retention time. The injection point for a compound was marked on the chart paper by instant switching of the ionization voltage. All peaks were sharp and symmetrical; chart speed was so adjusted that retention distances were more than 4 cms. Pure hydrocarbons including the normal paraffins were injected in the exact sequence of their elution times. As a proof of accuracy of experimental data, logarithm of corrected retention distances of the normal paraffins against carbon numbers showed excellent straight line fit in all cases.

2,3-dimethylpentane, 3-methylhexane, 3-methylheptane, 2-methyloctane, 2-methylheptane and 4-methylnonane were obtained as a gift from Dr. R. R. Wilson of the Associated Octel Co. Ltd., London, while the other hydrocarbons were purchased.[†]

Retention indices in SE-30 and other liquid phases were calculated with the help of a semilog paper⁵ and were rounded to the nearest whole number. Accuracy in the data is within ± 1 index unit.

Results and Discussion

The relative retentions with respect to normal heptane of all types of hydrocarbons viz. aromatic, olefinic, cyclic and isoparaffins, have been found to give straight line plots with column temperature in SE-30 (Figs. IA & IB), but the slopes are in opposite directions. In general, compounds having relative retentions smaller than unity give positive slopes while others having the same greater than unity give negative slopes. This

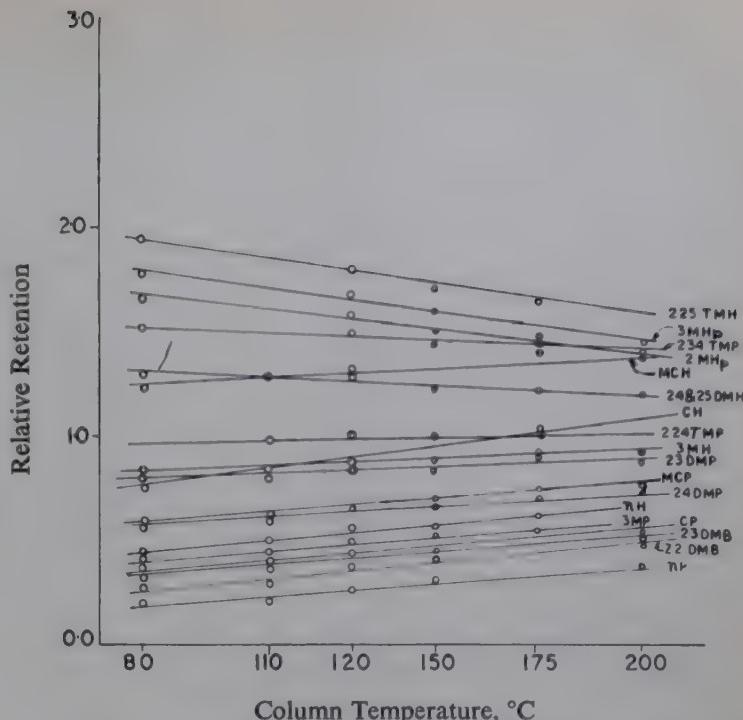


Fig. 1A—Plot of Relative Retention of Saturated Hydrocarbons against Column Temperature in SE-30

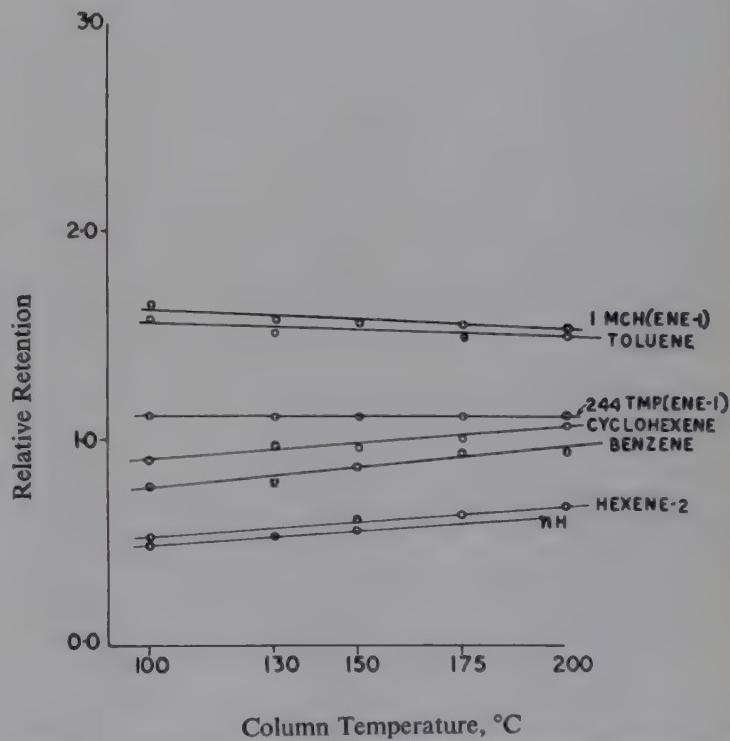


Fig. 1B—Plot of Relative Retention of Unsaturated Hydrocarbons against Column Temperature in SE-30

observation is in order with that of Bricoux and Duyc-kaert³ in high vacuum silicone grease (HVSG). From the data of Groebler⁶ it has been proved that specific retention volumes of normal paraffins in squalane vary linearly with column temperature (Fig. 2). It can be mentioned that the slopes in the plot of logarithm of corrected retentions of normal paraffins against their

**General Electric, USA.

†From Phillips Petroleum Co. of USA.

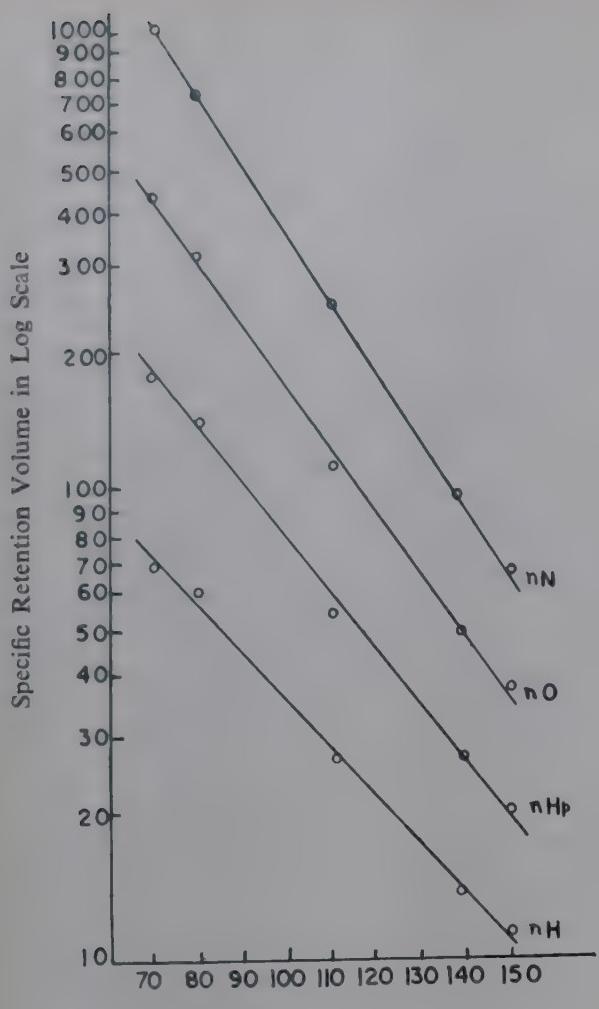


Fig. 2—Plot of Specific Retention Volume against Column Temperature (6)

carbon numbers vary with temperature and also with the nature of the stationary liquid. It is, therefore, expected that retention index of a compound (which is computed from the retention data of two normal paraffins between which the given compound elutes) will vary linearly with column temperature. Different stationary liquids will give different slopes. From the data reported by the Gas Chromatography Discussion Group⁷, Ettre and Billeb⁸ obtained linear I-T plots of hydrocarbons in squalane. The present authors have investigated about 40 hydrocarbons of all types in SE-30 in the range 80-225°C and obtained a good linearity of retention index with temperature (Figs. 3A & 3B) with a scatter of \pm index 1 unit in most cases and \pm 2 in a few. Linear plots were also obtained in Figs. 4A and 4B with saturated hydrocarbons in dinonylphthalate⁷ (DNP) and high vacuum silicon grease⁹. A strongly polar liquid phase namely polyethylene glycol-400 (PEG)⁷ gave linear plot (Fig. 4C) with polar hydrocarbons (with higher aromatics the randomness is within \pm 3 index units). Ettre and

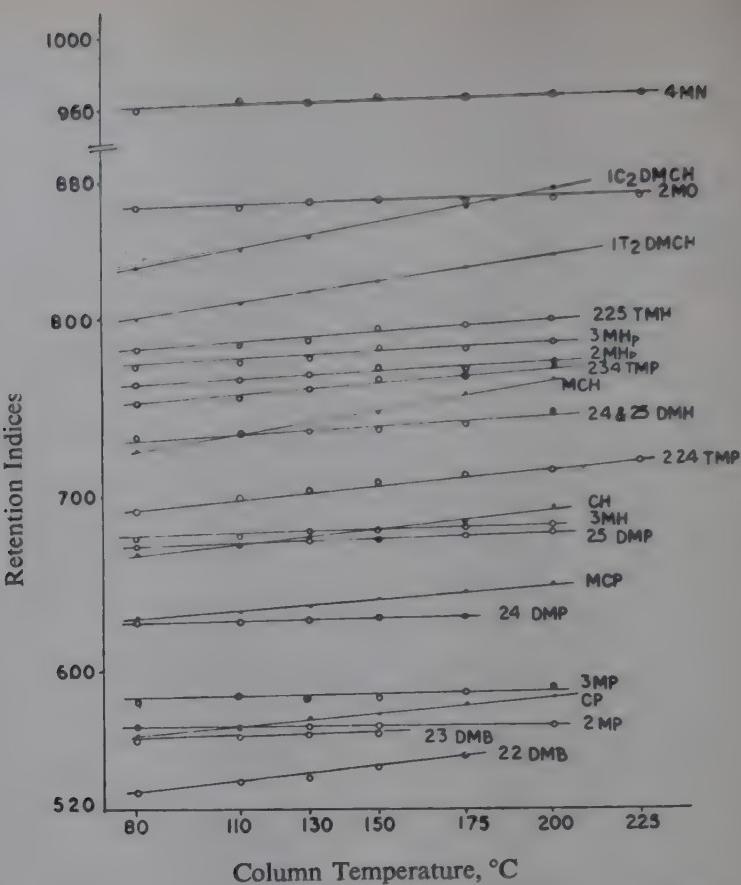


Fig. 3A—I-T Plot of Saturated Hydrocarbons in SE-30
[Please read 23 DMP in place of 25 DMP]

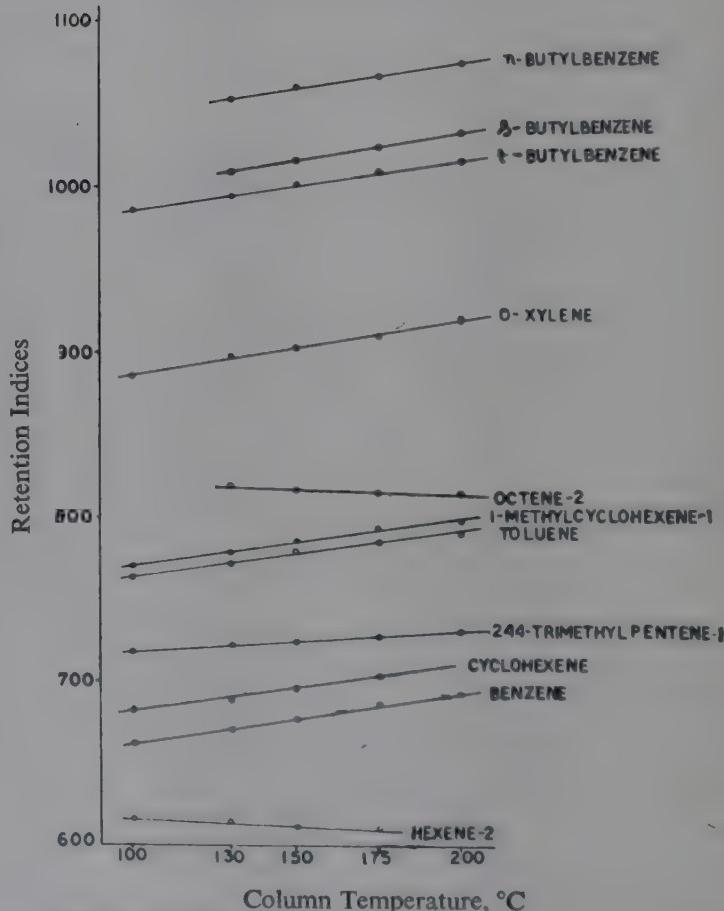


Fig. 3B—I-T Plot to Unsaturated Hydrocarbons in SE-30

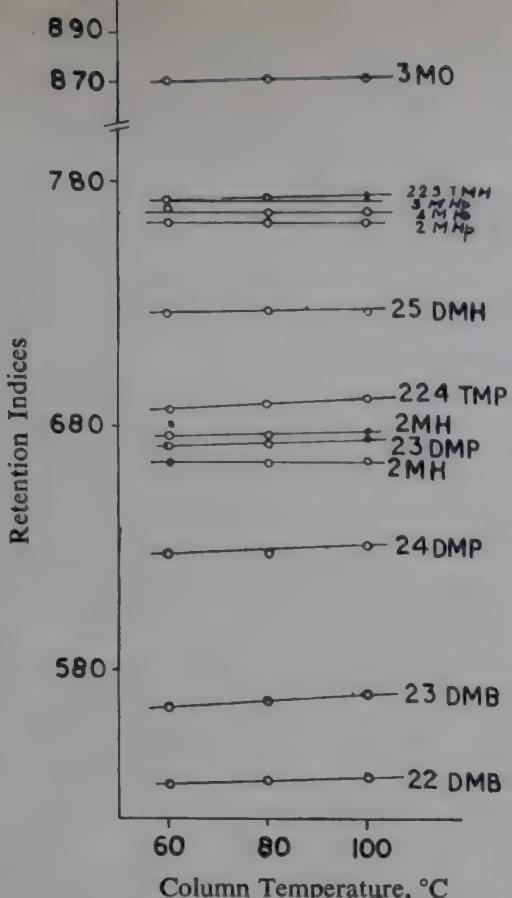


Fig. 4A—I-T Plot of Alkyl Paraffins in D.N.P. (7)
[Please read 3MH in place of 2 MH]

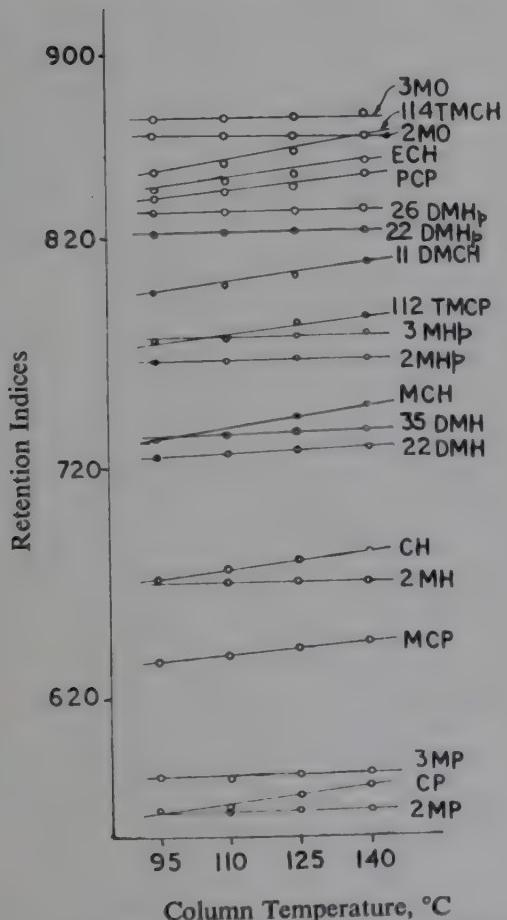


Fig. 4B—I-T Plot of Saturated Hydrocarbons in H.V.S.G. (3)
[Please read 25DMH in place of 35 DMH]

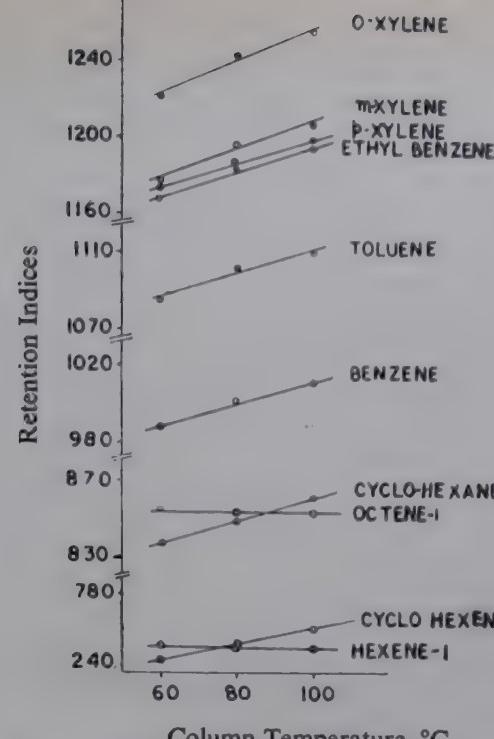


Fig. 4C—I-T Plot of Unsaturated Hydrocarbons in P.E.G. 400 (7)

Billeb⁴ observed that the available data on polar solutes like the ketones, esters, and alcohols give a linear fit when one assumes a scatter in the indices of ± 3 units. Linearity of I-T plot is a phenomenon not restricted to a single stationary liquid or to saturated hydrocarbons alone, but is considered a general rule for all partitioning liquids and solutes of all types. Obviously, this phenomenon deserves detailed investigation especially with respect to developing new parameters for subclassification of hydrocarbons and characterization of peaks in complex chromatograms.

Subclassification of Hydrocarbons: Perhaps the most important use of I-T plots is their utilization in the classification of hydrocarbons into types. Subtraction techniques in GC are known for olefins, aromatics and normal paraffins but not for other types of hydrocarbons. It has been observed that slopes of I-T plots when divided by the carbon number 'n' of the lower normal paraffins (used in the calculation of I) exhibit a characteristic pattern for various hydrocarbon types. For example, in SE-30 $\frac{dI/dT \times 10^3}{n}$ values (Table 2) for

mono- and di-alkyl paraffins lie between 2 and 10, for trialkyl paraffins between 16 and 26, for cycloparaffins from 30 to 45 and for aromatics from 30 to 50. Simple olefins exhibit the unique effect of negative slopes in SE-30 i.e. decrease of retention index with temperature. (In Tables 1A and 1B the values of n were taken at 95°C for HVSG and at 80°C for other liquid phases.)

However, with highly branched olefins and cyclo-olefins the slopes are positive and the effect of branching and cyclization are much stronger than that of unsaturation. Thus, 244-trimethylpentene -1 behaves like the trialkyl paraffins, cyclohexene and methylcyclohexene

like the cycloparaffins (Table 1). Thus from, $\frac{dI/dT}{n}$

values in SE-30, mono-, di- and trialkyl paraffins, simple olefins (branched and cyclo-olefins are exceptions) cycloparaffins and aromatics can be distinguished for group classification.

An examination of the values of $\frac{dI/dT}{n}$ (Tables 1A,

1B and 2) reveals that the efficiency of subclassification of hydrocarbons is dependent on the properties of liquid phases. An extensive study of this aspect might result in developing better stationary liquids not only for cleaner classification but also for distinction of individual hydrocarbons in a subclass. It appears from the

results (Table 1A, 1B and 2) that multi-column technique will prove more efficient than a single stationary liquid.

Characteristics of I-T plots: The rate of increase of retention index in non-polar liquids with temperature for hydrocarbons of comparable molecular weights has been found to follow the order: aromatic > cyclic > tetra-alkyl paraffins > di- and mono-alkyl paraffins. Normal paraffins by definition have constant values at all temperatures. Obviously some hydrocarbons will co-elute with one or more of other types. A few hydrocarbons having close index values as the normal paraffins may co-elute at certain temperatures. These cases may be differentiated as inversion phenomena. An examination of I-T plots reveals the possibilities of numerous inversion and co-elution temperatures. This phenomenon should be given due consideration in the identification of peaks in complex chromatograms in the isothermal or programmed temperature GC. Co-elution temperatures of a few common compositions have been given

TABLE 1A—TEMPERATURE COEFFICIENT OF RETENTION INDICES OF ALKANES IN POLAR AND NON-POLAR LIQUIDS

Name	Compound	Symbol	SE-30	SQ	$dI/dT \times 10^3$ in n	HVSG	DNP
2-Methylpentane		2 MP	3.2	2.0	0	—	—
3-Methylpentane		3 MP	8.1	4.7	7.3	—	—
2-Methylhexane		2 MH	—	3.3	4.8	5.5	—
3-Methylhexane		3 MH	5.4	5.0	—	8.5	—
2-Methylheptane		2 MHp	8.6	1.4	4.8	4.8	—
3-Methylheptane		3 MHp	9.1	2.9	5.7	8.1	—
2-Methyloctane		2 MO	2.1	—	0.0	—	—
3-Methyloctane		3 MO	—	—	7.5	6.3	—
4-Methylnonane		4 MN	3.1	—	—	—	—
3-Ethylhexane		3 EH	—	3.3	—	—	—
2, 2-Dimethylhexane		22 DMH	—	8.2	12.7	—	—
2, 5-Dimethylhexane		25 DMH	10.5	4.7	17.0	13.0	—
2, 2-Dimethylheptane		22 DMHp	—	—	8.0	—	—
2, 6-Dimethylheptane		26 DMHp	—	—	6.9	—	—
2, 2-Dimethylbutane		22 DMB	—	18.0	—	—	14.5
2, 3-Dimethylbutane		23 DMB	4.5	14.3	—	—	23.0
2, 3-Dimethylpentane		23 DMP	7.1	6.7	—	—	16.6
2, 4-Dimethylpentane		24 DMP	3.4	5.5	—	—	8.3
3, 3-Dimethylhexane		33 DMH	—	18.0	—	—	—
2, 3-Dimethylhexane		23 DMH	—	10.0	—	—	—
3, 4-Dimethylhexane		34 DMH	—	13.7	—	—	—
2, 2-Dimethylpentane		22 DMP	—	6.0	—	—	—
2, 4-Dimethylhexane		24 DMH	10.5	9.5	—	—	—
2, 3, 3-Trimethylpentane		233 TMP	—	29.7	—	—	—
2, 2, 3-Trimethylpentane		223 TMP	—	24.6	—	—	—
2, 2, 4-Trimethylpentane		224 TMP	25.8	16.7	—	—	20.8
2, 3, 4-Trimethylpentane		234 TMP	21.7	24.4	—	—	—
2, 2, 5-Trimethylhexane		225 TMH	16.5	9.5	—	—	—

TABLE 1B—TEMPERATURE COEFFICIENT OF RETENTION INDICES OF CYCLIC AND UNSATURATED HYDROCARBONS IN POLAR AND NON-POLAR LIQUIDS

Name	Compound	Symbol	d I/dT × 10³ in n		
			SE-30	SQ	PEG-400
Cyclopentane	CP	34.6	34.0	50.0	—
Methylcyclopentane	MCP	31.7	30.0	34.2	—
Cyclohexane	CH	35.4	37.8	49.1	64.3
Methylcyclohexane	MCH	44.4	35.7	47.1	—
1 trans 2-Dimethylcyclohexane	1T₂DMCH	34.3	35.7	—	—
1 cis 2-Dimethylcyclohexane	1C₂DMCH	42.5	—	—	—
1, 1, 2-Trimethylcyclopentane	112TMCP	—	—	38.1	—
1, 1-Dimethylcyclohexane	11DMCH	—	—	35.4	—
n-Propylcyclopentane	n PCP	—	—	33.1	—
Ethylcyclohexane	ECH	—	—	36.6	—
1, 1, 4-Trimethylcyclohexane	114TMCH	—	—	44.9	—
n-Propylcyclohexane	n PCH	—	—	40.0	—
Hexene-2		-16.3	—	—	—
Octene-2		- 9.8	—	—	—
2, 4, 4-Trimethylpentene-1	244 TMP (ene-1)	15.4	—	—	—
Cyclohexene		44.8	—	—	72.0
1-Methylcyclohexene-1	1-MCH (ene-1)	39.8	—	—	—
Benene		49.1	58.3	—	66.0
Toluene		36.0	47.6	—	61.2
O-Xylene		38.5	—	—	62.5
t-Butylbenzene		30.8	—	—	—
s-Butylbenzene		32.6	—	—	—
n-Buylbenzene		30.0	—	—	—
Ethylbenzene		—	—	—	62.7
p-Xylene		—	—	—	60.0
m-Xylene		—	—	—	63.4
Heptene-1		—	—	—	0.0
Octene-1		—	—	—	0.0

TABLE 2—SUB-CLASSIFICATION OF HYDROCARBONS

Hydrocarbon Types	Range of d I/dT × 10³ Values in n				
	SE-30	SQ	HVSG	DNP	PEG-400
Monoalkylparaffins	2-9	2-10	0-8	5-9	—
Dialkylparaffins	3-11	6-18	7-13	8-23	—
Trialkylparaffins	16-26	10-30	—	10-21	—
Simple olefins	negative	—	—	—	0
Cyclo-olefins	40-45	—	—	—	70
Cycloparaffins	32-45	30-38	33-50	—	60
Aromatics	30-50	48-58	—	—	60-65

TABLE 3—COMPARISON OF CO-ELUTION CHARACTERISTICS IN NON-POLAR LIQUID PHASES

Co-elution Compositions	SE-30		SQ		HVSG	
	°C	I	°C	I	°C	I
CP, 23 DMP	78	561	65	567	—	—
CP, 2 MP	115	568	73	570	95	571
CP, 3 MP	222	588	167 ^e	590	170 ^e	588
MCP, 24 DMP	60 ^e	628	65	630	—	—
CH, 2 MH	—	—	71	667	88 ^e	669
CH, 23 DMP	117	673	96	673	—	—
CH, 3 MH	150	680	133 ^e	680	—	—
MCH, 24 DMH	108	733	85	735	—	—
MCH, 25 DMH	108	733	62	729	95	733
MCH, 2 MH _p	267 ^e	784	206 ^e	766	203 ^e	770
MCH, 3 MH _p	330 ^e	805	255 ^e	779	245 ^e	783

e—stands for extrapolated values.

in Table 3 in three liquid phases, and for some more cases which were available only with squalane in Table 4.

It can be seen from these tables that for a given co-elution composition, the order of co-elution temperature is SE-30 > HVSG > squalane. An approximate prediction of co-elution temperatures for all compositions (Tables 3 and 4) might be possible in any other stationary liquid by comparing the nature of shift in co-elution temperature for a few cases with squalane. An examination of results (Tables 3 and 4) shows that co-elution among isomeric alkanes is quite common but has certain restrictions between cycloalkanes and alkanes. For example, cyclo-paraffins and mono and di-alkyl cycloparaffins do not co-elute with isomers from alkyl paraffins, but tri-alkyl cycloparaffins can co-elute with alkanes of equal carbon numbers (e.g. 112 TMCP and 3 MH_p 114 TMCH and 2 MO, in HVSG). In general, cycloparaffins (except tri- and higher substituted ones) co-elute with alkanes containing one more carbon atom (Fig. 3A.).

Other workers^{3,4} have illustrated the principle of choosing column temperature for the best possible resolution of a given mixture in a stationary liquid. In addition to the principle of peak shifting technique³, there is still scope for new methods of peak identification based on co-elution phenomenon. For example, in order to confirm whether a peak is 23 DMB or 2 MP or 3 MP is to run the chromatogram, along with CP as an additional component at 78, 115 and 222°C in a SE-30 column. If the compound is 23 DMB there will be a single peak at 78°C but double peaks at other temperatures. CP and 2 MP will show single peak at

115°C but double peaks at all other temperatures and so on (Table 3).

TABLE 4—CO-ELUTION CHARACTERISTICS IN SQUALANE PHASE^a

Co-elution* Compositions	°C
MCP, 22 DMP	34
233 TMP, 23 DMH	70
233 TMP, 2 MH _p	75
233 TMP, 4 MH _p	89
2M3EP, 23 DMH	25
2M3EP, 2 MH _p	76
34 DMH, 3 MH _p	78
3 M3EP, 3 MH _p	40
3M3EP, 225 TMH	68
33 DMP, 2 MH	133 ^e
33 DMP, 23 DMP	200 ^e
MCH, 223 TMP	182 ^e
MCH, 33 DMH	195 ^e
MCH, 4 MH _p	230 ^e
MCH, 23 DMH	233 ^e
MCH, 3 MH _p	255 ^e
223 TMP, 4 MH _p	257 ^e
223 TMP, 2 MH _p	220 ^e
33 DMH, 2 MH _p	217 ^e
234 TMP, 23 DMH	124 ^e
234 TMP, 2 MH _p	130 ^e
234 TMP, 4 MH _p	152 ^e
234 TMP, 3 MH _p	190 ^e
234 TMP, 225 TMH	250 ^e
23 DMH, 2 MH _p	130 ^e
23 DMH, 4 MH _p	218 ^e
34 DMH, 225 TMP	160 ^e
233 TMP, 3 MH _p	115 ^e
233 TMP, 34 DMH	140 ^e
233 TMP, 225, TMH	145 ^e

*Symbols follow the pattern of Table 1.

e—stands for extrapolated values.

This principle can be extended by employing a proper cycloparaffin as additional component to co-elute with any isoparaffins at temperatures upto the highest limit of a stationary liquid. Hence a cycloparaffin can be used to identify its co-elution counterpart in a given stationary liquid within its working limit of temperature. An examination of results (Tables 1A, 1B and 3) reveals a potential application in the classification of stationary liquids (i) by properly selecting one or more compounds

which will give widely differing values of $\frac{dI/dT}{n}$ with

partitioning liquids of different polarity and (ii) by choosing a few pair of solutes which will give considerable shift in co-elution temperature in different stationary liquids.

Vapour Pressure and Co-elution Phenomenon: Vapour pressures of hydrocarbons increase with temperature but not linearly. Hence, the ratio of retention index to vapour pressure of a hydrocarbon does not show linear variation with temperature. In a previous paper⁸, the present authors have shown that in general a hydrocarbon, irrespective of the type which has a higher vapour pressure, gives a lower index value in non-polar liquids. This rule has numerous exceptions. The phenomenon of co-elution shows more clearly how the separation of non-polar solutes like hydrocarbons even in a non-polar liquid is dependent on structural features of solute molecules. In other words, vapour pressure fails to explain the co-elution phenomenon, for example methyl cyclopentane and 2,4 di-methylpentane co-elute at 65°C in squalane, their vapour pressures at this temperature are 610 and 480 mm. of mercury respectively. Conversely, cyclohexane and 2,4 -dimethylpentane have almost the same vapour pressure-temperature curve, nevertheless, they can be easily separated in SE-30 (or in any other non-polar liquid phase) without having any co-elution in the range of 80 to 300°C.

Conclusions

- (i) Linearity of the variation of I with T is characteristic of all types of hydrocarbons in non-polar as well as polar stationary liquids;
- (ii) a new parameter derived from slopes of I-T lines has the potentiality to classify hydrocarbons into several types;
- (iii) I-T plots can be utilized successfully in confirming the identity of many hydrocarbon peaks;
- (iv) the phenomenon of peak inversion and co-elution must be taken care of in interpreting complex chromatograms and in determining the best column temperature for the separation of a given mixture;
- (v) further investigation into the temperature coefficient of retention index and coelution phenomenon is likely to give a method of classification for the stationary liquids;
- (vi) it is suggested that the index values be given in at least three column temperatures for the sake of maximum information.

Acknowledgement

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Salt-Coated Silica Gel Supports in the Gas Chromatography of Saturated Hydrocarbons*

By

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The object of this study is to develop efficient gas chromatographic supports from silica gel in order to substitute the expensive and imported diatomaceous types. A method of modification of the three-dimensional pore structure of silica gel based on coating it with inorganic salts of transition metals followed by heating in a muffle furnace to about 1000°C has been developed. Copper sulphate has been found to cause sixteen-fold reduction in surface and eleven-fold increase in mean pore diameter of silica gel. These salt-coated supports show a drastic reduction in the heat of adsorption of saturated hydrocarbons, i.e. they facilitate higher desorption rate. The elution power with symmetric peaks increases with pore-widening and hence for the best resolution of sample components of a given range of size and shape, silica gel of a specific pore size distribution will be required. The elution of saturated hydrocarbons from these supports is not in accordance with vapour pressure but depends strongly on the molecular structure. Cycloparaffins always elute much ahead of the normal paraffins of equal carbon numbers, probably due to a greater closeness of approach towards the adsorbent surface of all the carbon atoms of the normal paraffins. Separation of *cis*- and *trans*-isomers is poorer with salt-coated supports than with most stationary liquids. The salt coated silica supports exhibit a peculiar co-elution phenomenon, namely a hydrocarbon can co-elute with another more than once (unlike any stationary liquid). With respect to speed of analysis, the salt-coated silica supports compare favourably with non-polar liquids like SE-30. A C₅-C₁₀ normal paraffins sample can be completely resolved in less than two minutes from a 3 feet column packed with this support. Although the cation plays a major role in the modification of silica gel texture, the function of counterpart anion or ligand is also important. From the gas chromatographic point of view copper sulphate gives far superior silica support to copper-ammonium sulphate probably due to release of a larger volume of gas in the 700-950°C range by the former as is evident from thermogravimetric analysis.

The growing popularity of gas chromatography (GC) as a unique separation technique in laboratory and industry merits a strong programme of developing the main consumable item, namely, the solid support from indigenously available raw materials. At the present the imported and very expensive diatomaceous supports are used in GC. Silica gel has good potential for efficient gas chromatographic supports.

It is known that the surface hydroxyls of silica xerogels have practically no effect on the adsorption energies of saturated hydrocarbons with σ -bonds. The forces of interaction between non-specific adsorbents like dehydroxylated silica gels and non-specific adsorbates are

mainly of the London dispersion type. In such cases, the retentive mechanism of GSC columns will be determined by the geometrical details of three-dimensional porous structure of the adsorbents and by the polarizabilities and mean free paths of the adsorbate molecules. According to Kiselev¹ et al, the adsorption of solute at very low levels of concentration, as employed in GSC, is very selective, i.e. different molecular species of solute components are retained on sites (pores of specific dimensions) which are most active for the given type of adsorption. Hence, an adsorbent with a specific distribution of pore geometry will give best resolution of a sample of certain molecular range of saturated hydrocarbons. It also follows that different molecular species will lose their momentums to different extents during their passage through the adsorbents (with pore dimensions of 15 to 5 times that of solute molecules) by

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collision with pore walls. When pore dimensions start falling down from about 5 times the molecular dimensions, molecular sieving action begins. Therefore, a wide range of selectivities is possible in GSC by utilizing pore size and shape as variables. Since silica gel can offer a wide variation in the spectrum of pore specifications it has been chosen as a GSC support in the present investigation.

It can be mentioned that the pore structure of silica gel is very sensitive to methods of preparation and to post treatments. Imelik and Carteret² have described a method of controlling pore size by precipitating silica gel from solutions of sodium silicate with formaldehyde, but there is no report on their application in GSC.

Kiselev¹ et al have developed a hydrothermal technique to such a perfection that by autoclaving a silica gel (of surface area 375 m²/g and of average pore diameter 104 Å) under strictly controlled conditions of steam pressure and temperature they succeeded in preparing samples of practically any reduced surface down to 6.6 m²/g. and to any increased pore diameter upto 4100 Å. They have made extensive studies on the gas chromatographic properties of these supports. Schultze and Schmidt-Kuster³ have used calcination upto 800°C for making wide pore silica for the separation of hydrocarbon gases. Huber and Keulemans⁴ developed a silica support by heating to 950°C for 15 hours which gave efficient separation of normal paraffins. But by heating alone, silica gels cannot be changed much in surface and pore diameter^{5,6}.

For separation of large molecules, which require considerably wide macro-porous silica, the present authors have considered the thermal treatment of silica xerogels, previously coated with inorganic salts, as a suitable method. There are a very few information^{7,8} on the changes of texture of silica gels by heating with foreign adsorbed cations. Alkali and alkaline-earth cations reduce surface and increase pore size, whilst iron and nickel ions actually cause a slight increase in surface area. Certain cations give wider pores at the cost of the smaller ones, whilst others engender wide pores without affecting the small ones. In this study copper

salts have been used as a modifier of silica gel texture. Imelik⁷ et al have shown that by heating silica gel with adsorbed cupro-ammonium sulphate the transition temperature of amorphous to crystalline structure is considerably lowered and also there is a change in the crystallized phase. It is considered likely that prolonged thermal treatment with copper ions will change the globular dimensions of the micro-crystallites as well as their degree of packing. These and other changes in the texture of silica gels will no doubt affect the gas chromatographic behaviour of saturated hydrocarbons.

Experimental

A commercial silica gel of 60/80 mesh (B.S.S.) was washed several times with hot concentrated hydrochloric acid until no yellow coloration was observed. It was then washed free of chloride ions with distilled water and oven-dried at 200°C. Three supports were prepared from this purified gel in the following manner respectively: (1) by heating in a muffle furnace for several hours at about 1000°C with occasional stirring, (2) by coating a solution of copper sulphate (0.117 g. Cu/g. SiO₂) by the conventional evaporation procedure followed by heating as in (1); and (3) by coating with a solution of cupro-ammonium sulphate (0.117 g. Cu/g. SiO₂) followed by thermal treatment as in (1).

Another support was prepared from Chromosorb W, 100/120 mesh by the same procedure followed for support (3). After removing from the muffle furnace the supports were cooled in a desiccator, then packed in a cleaned and dried copper refrigeration tubing (1/8" O.D., 3' or 5' long) regularly tapping with a rubber-padded glass rod.

An Aerograph Hi-Fi-600 D Gas Chromatograph fitted with a flame ionization detector was used in this investigation. The carrier gas was argon and a flow rate of 30 cc./min. was maintained at the detector jet in all experiments.

Results and Discussion

Evidence of Pore Widening: (a) *From Texture:* Surface area, pore volume and mean pore radius for four silica samples have been obtained (Table 1). It is noted that

TABLE 1—COMPARISON OF TEXTURES OF SILICA GEL PREPARATIONS

Support	Symbol	Pore Volume, cm ³ /g.	Specific Surface Area, m ² /g.	Mean Pore radius Å	Reduction in surface Area, m ² /g.
Silica Gel (Starting material)	SG	0.480	375	25	1.0
Heated Silica Gel	SG-H	0.545	296	36	1.3
Cupro ammonium Sulphate Coated Silica Gel	SG-CAS	0.284	29	194	13.0
Copper Sulphate Coated Silica Gel	SG-CS	0.477	24	398	15.6

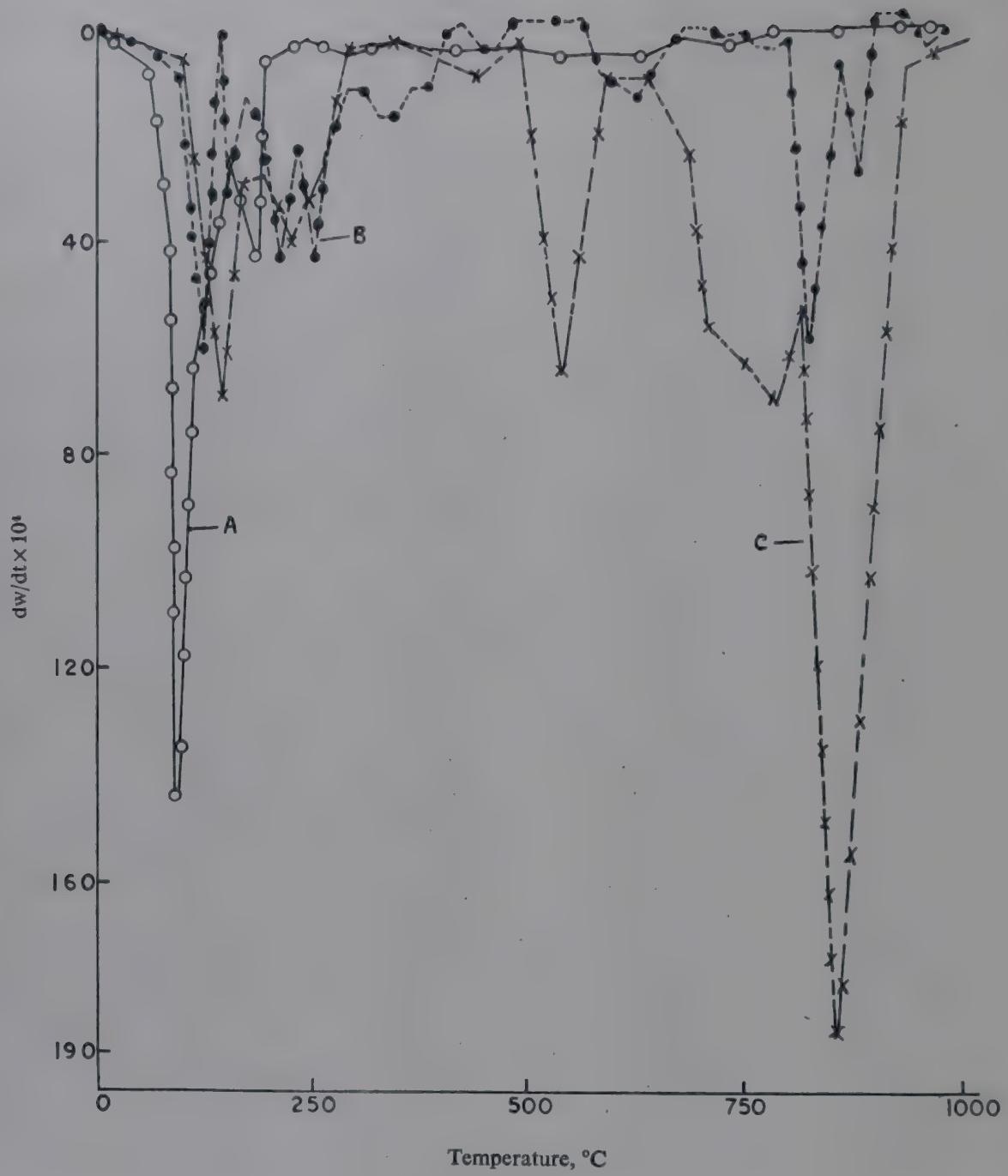


Fig. 1

A—D.T.G.A. Plot of Silica Gel

B—D.T.G.A. Plot of Cupro-Ammonium Sulphate on Silica Gel

C—D.T.G.A. Plot of Copper Sulphate on Silica Gel

thermal treatment alone causes slight change in surface area and pore diameter compared to heating in presence of copper salts. The significant difference in the texture of silica gels by copper sulphate and cupro-ammonium sulphate is indicative of some role by the anion or ligand counterpart. Extensive research is needed to define the exact function of cations and anions of various coating salts and to study the effects of details of heating procedure in order to get a clear insight into the three-dimensional porous structure of silica gels.

The mechanism of pore broadening proposed by Kiselev⁹ is based on the concept of corpuscular nature of silica particles. This hypothesis is well-supported by Janak's¹⁰ electromicrographs of a typical silaceous GLC support, namely, Sterchamol where the silica globules formed space-linked chains with free inter-spaces which account for as much as 95 per cent of surface area. Heating in presence of copper salts has probably helped further agglomeration of primary globules through inter-particle dehydroxylation reaction.

(b) *From Thermogravimetric Analysis:* The derived thermogravimetric analysis (DTGA) curves for the silica samples have been shown in curves 1A, 1B and 1C of Fig. 1 and TGA curves in 2A, 2B and 2C of Fig. 2. Some difference in these curves can be readily noticed. The release of a large volume of vapours with great force is likely to cause a larger pore widening. With SG-CAS, the total weight-loss is 22 per cent compared to 20 per cent with SG-CS; but the mean pore diameter is larger in the latter support. This might have relation with the escape of a much larger amount of vapour from the pores of copper sulphate treated silica in the temperature range of 700-950°C (as is evident from the comparison of Figs. 1B with 1C). Mention may be made about the retardation of physi-sorbed water peak towards higher temperatures in the order of heated silica > copper ammonium sulphate-silica > copper sulphate treated silica.

(c) *From Heats of Adsorption:* The gas chromatographic method of determination of heats of adsorption is based on the equation.—

$$V_g = - \frac{\Delta H_a}{RT} + C$$

where V_g is the retention volume per unit weight of adsorbent at the column temperature T , H_a is the heat of adsorption and C is a constant.

Hence the slopes of linear plots of logarithm of corrected retention time against reciprocal of column temperature will be proportional to the heats of adsorption. The slopes of three normal paraffins have been given

in Table 2. According to Kiselev¹ et al the narrowing of pores increases the heats of adsorption of normal alkanes. It is therefore, evident from the results (Table 2) that SG-CAS has larger average pore diameter than SG-H.

TABLE 2—HEATS OF ADSORPTION OF NORMAL PARAFFINS IN SILICA SUPPORTS

n-Paraffin	Slope of log tR Vs. $1/T$ plot in	
	SG-H	SG-CAS
Nonane	2.13	1.87
Octane	2.09	1.70
Heptane	1.96	1.60

(d) *From Elution Capacity:* In the case of non-specific adsorbents like the dehydroxylated silica and non-specific adsorbates like the saturated hydrocarbons, a support having wider pores will elute comparatively larger molecule with symmetric peaks. It can be seen from Table 4 that at any given temperature SG-CAS has a stronger elution power than the heated silica support. It has also been observed that the copper sulphate-treated material possesses the highest elution capacity among these silica supports. For example, normal decane is eluted symmetrically from SG-CS support at 175°C but not from SG-CAS column. There-

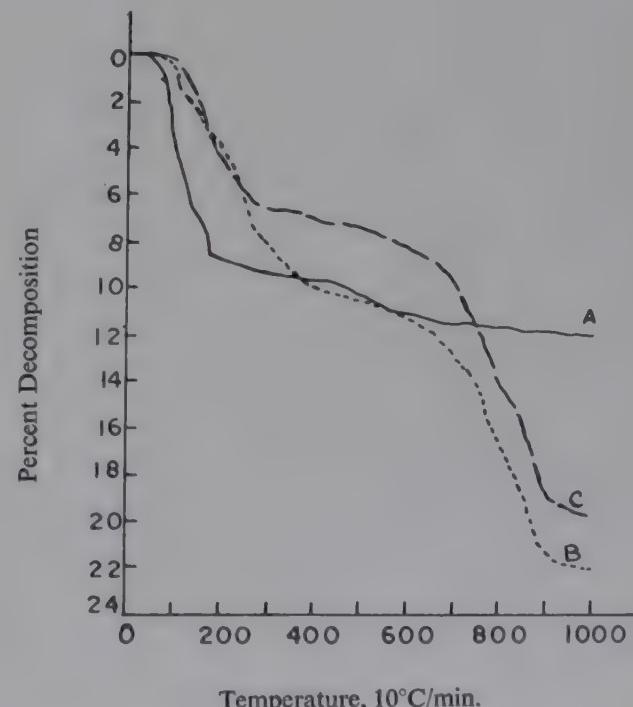


Fig. 2
A—T.G.A. of Silica Gel
B—T.G.A. of Silica Gel Coated with Copper Ammonium Sulphate
C—T.G.A. of Silica Gel Coated with Copper Sulphate

TABLE 3—LINEAR ELUTION BEHAVIOUR OF HYDROCARBONS FROM SILICA COLUMNS

Heated Silica Gel							
Largest Molecules with Symmetrical Peaks	Temp., °C	Smallest Molecule with Tailing	Temp., °C	Largest Molecules with Symmetrical Peaks	Temp., °C	Smallest Molecule with Tailing	Temp., °C
n-Hexane	175	n-Heptane	175	n-Pentane	75	n-Hexane	75
n-Heptane	200	2,4-Dimethylpentane	175	Methylcyclopentane	75	3-Methylpentane	75
1-cis 2-Dimethyl cyclohexane	200	n-Octane 2,2,5-Trimethylhexane	200	n-Hexane 2,4-Dimethylpentane	100	2,3-Dimethylpentane	100
1-trans 2-Dimethyl cyclohexane	225	1-cis 2-Dimethyl- cyclohexane	225	2,2,4-Trimethyl- pentane	100	n-Heptane	100
n-Octane 2,2,5-Trimethylhexane	250	n-Nonane	250	n-Heptane 2,2,5-Trimethylhexane	150	2,4 & 2,5-Dimethylhexane	150
	250			n-Nonane	150	n-Hexane	150
				n-Decane	175	n-Octane	150
					200	4-Methylnonane	175
					225		200

fore, the pore structure of the silica-based supports is in the same order as noted in Table 1. The original silica gel irreversibly adsorbed even methane at 175°C. Improvement of elution power, particularly of the salt-coated silica, with increase in column temperature is due to increased thermal energy input of the solute molecules i.e. with the consequent lowering of their mean free paths. The order of supports with respect to their pore structure is also corroborated by the results in (Table 4).

TABLE 4—COMPARISON OF CORRECTED RETENTION TIMES OF NORMAL PARAFFINS UNDER STANDARD CONDITIONS OF FLOW RATE AND COLUMN DIMENSIONS AT 175°C

Compound	Corrected Retention Times (secs) at 175°C in			
	SG-H	SG-CS	SG-CAS	SE-30
n-Hexane	49.4	2.0	18.8	4.4
n-Heptane	81.0	4.8	34.5	7.1
n-Octane	154.0	10.0	63.3	12.5
n-Nonane	314.6	19.4	110.7	19.1
n-Decane	631.0	33.9	208.0	30.4

In this table retention data corrected for gas hold-up at equivalent linear flow velocities have been compared, in order to cancel out effects due to column permeability and unequal zone velocity. The standard column dimensions of 5' × 1/8" O.D. have been assumed. As regards another important support characteristic, namely, the speed of analysis, it can be noted from Table 4 that the copper sulphate-treated silica is about 6 to 8 times better than the complex salt coated one, which in turn is about 2 to 3 times superior to the heated

silica. It is noticed (Table 4) that copper sulphate-silica will give somewhat faster analysis for lower hydrocarbons upto 9 carbon atoms than a typical non-polar liquid like SE-30; for larger molecules upto about 12 carbon atoms it appears that the speed of analysis will be comparable.

For still bigger hydrocarbon molecules highly macroporous silica gels will have to be developed. Alternatively, silica columns will require a comparatively higher temperature (and there is no restriction to using high temperature with silica or other GSC supports unlike stationary liquids, so long as the desired separation is obtainable). It can be pointed out from the results (Table 4) that SG-CS has superior selectivity towards normal paraffins (possibly for other saturated alkanes and cycloalkanes) than SE-30.

Comparative Performance of Silica Supports and Stationary Liquids: Two silica supports have been compared with a polar stationary liquid with respect to relative retention and Kovats' retention index^{12*} (Table 5A). The order of elution of alkyl paraffins listed in Table 5A is according to boiling points in SE-30¹³ and also in bis-ether¹⁴ with the exception of 2-methyl pentane. But in the silica supports retention is far more strongly determined by structural features than by vapour pressures of solute molecules. Comparing the separation factors (i.e. ratio of retentions) of isomeric alkanes it

*The definition of retention index (I) is given by the equation.

$$I = 100 \frac{\log t_X - \log t_N}{\log t_{N+1} - \log t_N} + 100 N$$

where 't' stands for retention data (time, distance or volume) corrected for column hold-up. The compound X elutes between two normal paraffins of carbon atoms N and N+1.

TABLE 5A—COMPARISON OF SELECTIVITIES OF HYDROCARBONS IN POLAR AND NON-POLAR STATIONARY LIQUIDS WITH SILICA SUPPORTS

Compound	B.P., °C	SG-H at 225°C		SG-CAS at 150°C		SE-30 at 110°C ¹³		Bis (Propionitrile) ether at 25°C ¹⁴	
		Relative Retention	Retention Index	Relative Retention	Retention Index	Relative Retention	Retention Index	Relative Retention	Retention Index
n-Pentane	36.0	1.00	500	1.00	500	1.00	500	1.00	500
Cyclopentane	49.3	1.12	519	0.94	482	1.78	566	3.34	660
2,2 Dimethylbutane	49.7	1.79	604	1.53	565	1.37	536	1.31	531
2,3 Dimethylbutane	58.0	1.83	608	1.86	593	1.74	562	1.76	576
2-Methylpentane	60.3	1.66	589	1.78	586	1.80	568	1.60	563
3-Methylpentane	63.3	1.78	603	1.75	584	2.05	585	1.98	590
n-Hexane	68.0	1.77	600	1.94	600	2.33	600	2.12	600
Methylcyclopentane	71.8	1.69	593	1.75	584	2.92	633	4.48	700
2,4 Dimethylpentane	80.5	2.53	669	2.80	556	2.77	628	2.44	618
Cyclohexane	80.7	2.05	629	1.97	602	3.67	671	6.69	753
2,3 Dimethylpentane	89.8	2.98	700	3.31	682	3.70	672	—	—
3-Methylhexane	91.9	2.99	700	3.23	677	3.97	679	3.82	678
n-Heptane	98.4	2.93	700	3.77	700	4.66	700	4.48	700
Methylcyclohexane	100.9	3.15	711	3.50	680	5.52	734	9.01	792

seems that silica supports are somewhat inferior to both the stationary liquids. Of course, column temperature was not identical in all the cases. A remarkable difference can be noted in Table 5A between GSC and GLC, with respect to elution behaviour of cycloparaffins. Retention indices of cycloalkanes are always much lower (and in some cases they elute ahead of normal paraffins of equal carbon numbers) with silica supports unlike the GLC columns. It is to be noted that GLC was compared at much lower temperatures and Retention indices of cycloparaffins increase at the rate of 5 to 10 units per 25°C.

Another important observation in the separation of *cis*- and *trans*-isomers of cycloparaffins has been given in Table 5B. The salt-coated support gives poor separation compared to both heated silica and SE-30.

Subtractive Properties: All the three silica supports exhibited subtractive property towards unsaturated hydrocarbons; at 150°C they irreversibly adsorbed all olefins (ethylene is eluted by SG-H and SG-CS, but not by SG-CAS) and all aromatics, except benzene which elutes with bad tailing. It has been found with cuproammonium sulphate on Chromosorb W column of equivalent lengths that all olefins and aromatics containing upto 10 carbon atoms are eluted within a minute at 150°C. It is, therefore, obvious that the cause of subtractive property is in the silica gel. It is known that silica gel interacts with unsaturated compounds through

surface hydroxyl groups only. It has been found from TGA curves that all the three silica supports still have some tendency to lose weight even after heating to 950°C. It is possible that these silica supports contain a small amount of residual hydroxyls. That the content of residual hydroxyls is small is evident from the fact that the subtractive property of the silica supports disappears after about 200 injections of 5 to 10 μl vapours each. Regeneration of this subtractive property is also possible by heating the columns to about 350°C. The capacity for adsorbing unsaturates permanently has been found to be much more with SG-CAS than with SG-H and SG-CS. All the three supports have been found to adsorb

TABLE 5B—COMPARISON OF SEPARATION CHARACTERISTICS OF CIS AND TRANS CYCLOPARAFFINS

Compound	SE-30 at 175°C I	Heated Silica at 175°C I	Cuproammonium Sulphate at 175°C I
1 <i>trans</i> - 2-Dimethyl- cyclohexane	828	773	775
1 <i>cis</i> - 2-Dimethyl- cyclohexane	863	790	777

irreversibly compounds containing oxygen functional groups and nitrogen heterocycles. The role of copper *vis-a-vis* the subtractive property is under investigation.

Effect of Column Temperature on Retention Indices: Variation of retention indices of alkyl paraffins (Fig. 3A) and of cycloparaffins (Fig. 3B) has been studied in the complex salt coated silica gel column at temperatures between 75 and 225°C. The effect of temperature on Retention Index¹² from this support is entirely different from GLC columns, which invariably give a linear increase. Notable features from Figs. 4A and 4B are that a compound can co-elute with another more than once and the separation of two adjacent hydrocarbons will have several maxima and minima. Mention may be made here that for the study of such sensitive parameters like retention indices in GSC columns the control of temperature should be within $\pm 0.5^\circ\text{C}$ and of flow within 0.1 per cent. But the control of temperature in the experiments reported in Figs. 4A and 4B was not better than $\pm 2^\circ\text{C}$.

Comparison of Few Silica Supports for Hydrocarbons Separation: Chromatograms of a mixture of normal paraffins containing 5 to 10 carbon atoms have been given in Fig. 4A from a 3' column of heated silica gel at 225°C and in Fig. 4B from a 5' column of cupro-ammonium sulphate treated silica at 150°C. The time of analysis is 2 minutes in Fig. 3A and about 6 minutes in Fig. 3B. Huber and Keulemans⁴ obtained the separation of C₅-C₁₂ normal paraffins in 10 minutes at 150°C from a column of silica gel heated to 950°C for 15 hours. Kiselev¹ et al completely resolved a mixture of C₆-C₁₇ n-alkanes at 260°C in 34 minutes from a silica gel prepared by hydrothermal treatment; column length was 100 cms. Peaks were symmetrical in all the four cases referred above. From a plot of logarithm of retention time against carbon number of the normal paraffins these supports can be compared with respect to speed of analysis. For example, the column and operating conditions used in (Fig. 4A) our work will require about 3 minutes for C₅-C₁₂ n-alkanes and about 23 minutes for C₆-C₁₇ n-alkanes; column used in figure 3B will require about 10 and 89 minutes respectively. If run under equivalent conditions of column lengths, temperature and flow the SG-CAS column will give faster analysis than that of SG-H.

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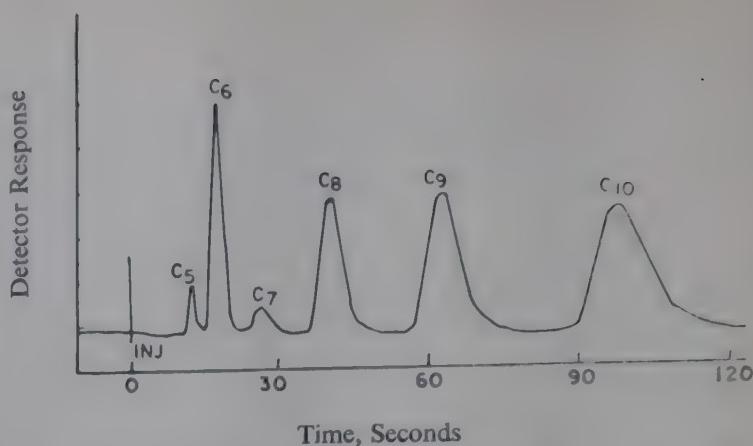


Fig. 3A—Separation of C₅-C₁₀ Normal Paraffins in Thermally Treated Silica Gel at 225°C

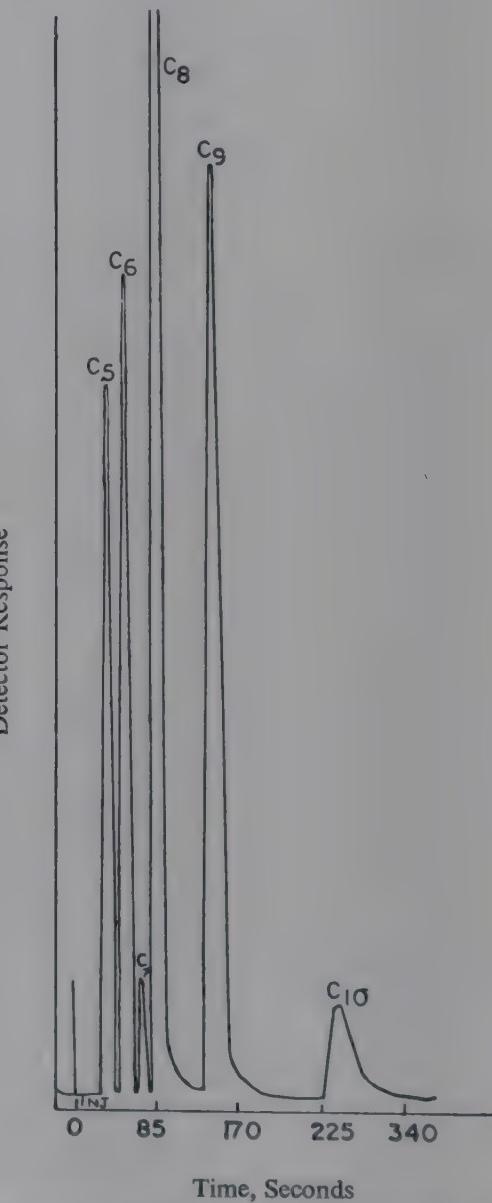


Fig. 3B—Separation of C₅-C₁₀ Normal Paraffins on Thermally Treated Cupro-Ammonium Sulphate on Silica Gel at 150°C

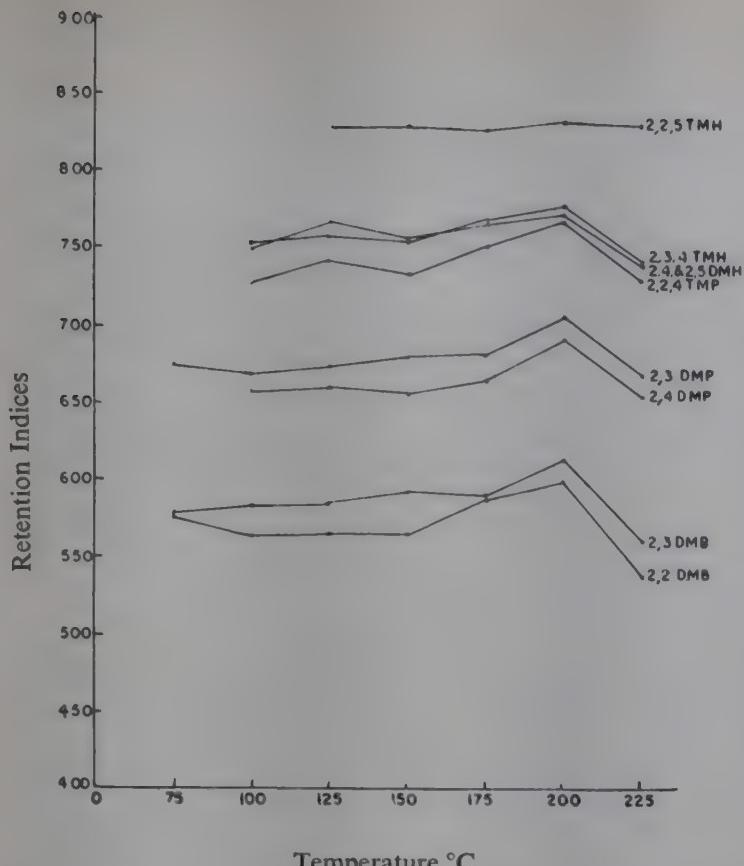


Fig. 4A—Effect of Temperature on Kovats Indices of Alkyl Paraffins in SG-CAS

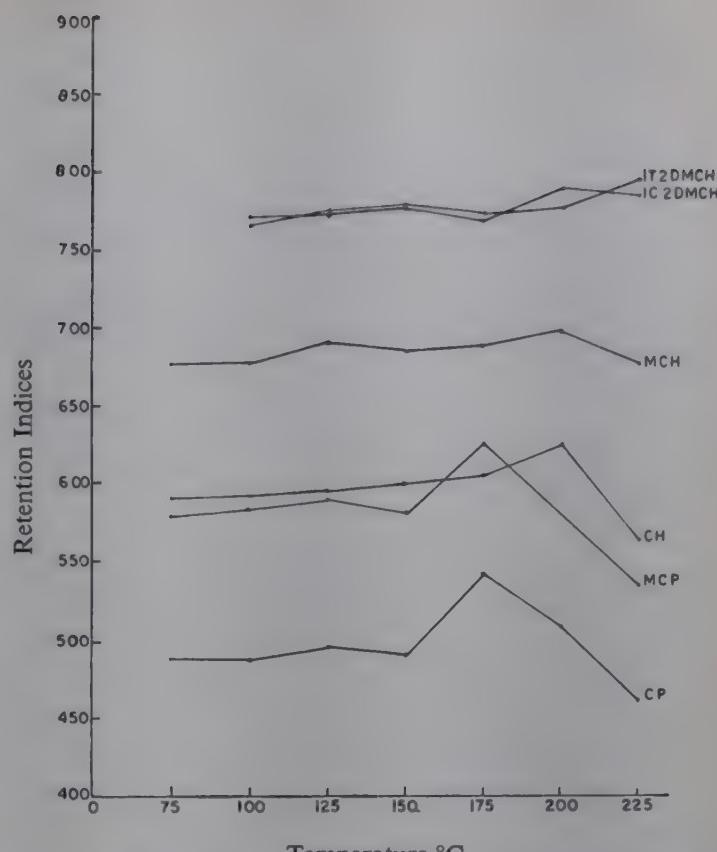


Fig. 4B—Effect of Temperature on Kovats Indices of Cycloparaffins in SG-CAS

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Chlorides of Ammonium and Potassium as Viscosity Depressants for Phosphonitric Nitrophosphate Slurry

By

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Potassium chloride and ammonium chloride have been found to lower appreciably the viscosity of the phosphonitric nitrophosphate slurry. Since they can be added in the form of solid they also cause a reduction in the percentage of moisture in the slurry. These additives may, therefore, be beneficially used for the smooth operation of the circulating pumps and the spherodizers in the process of manufacture of nitrophosphate.

In the manufacture of phosphonitric¹ nitrophosphate fertilizers by the reactions between (i) phosphate rock, (ii) nitric acid, (iii) ammonia and (iv) phosphoric acid (or ammonium phosphates) the reaction mixture in the plant passes through a series of reaction vessels, circulating pumps and spherodizers² in the form of a slurry. In the spherodizer, which is a specially designed rotary pelletizer-dryer, the slurry is sprayed against a falling curtain of dried, recycled fines. Drying is accomplished by hot gas at 204-260°C which is blown into the drum at about 25000 scfm. For the smooth operation of the plant in general and of the circulating pumps and the spherodizers in particular, viscosity of the slurry and its moisture content are to be kept as low as possible. To achieve this end, the effect of certain additives were studied. Ammonium chloride and potassium chloride were found to bring about this desired effect. Either of these can be added in the solid state to the slurry before it is sent for spraying in the spherodizer.

The viscosity studies have been conducted on the phosphonitric nitrophosphate slurry whose analysis is given in Table 1. The viscosity measurements were made by a rotating spindle type Brookfield Synchro-Lectric viscometer model LVT-E using spindle No. 2 at 30 r.p.m. The results of these measurements are given in Table 2.

The results show that the viscosity of the phosphonitric nitrophosphate slurry goes on decreasing as the

TABLE 1—ANALYSIS OF PHOSPHONITRIC NITROPHOSPHATE SLURRY (pH=7)

Component	Per cent
Ammoniacal N ₂	6.37
Nitrate N ₂	8.48
Water Soluble P ₂ O ₅	7.58
Citrate Soluble P ₂ O ₅	9.12
Citrate Insoluble P ₂ O ₅	Traces
Moisture	29.30

TABLE 2—EFFECT OF AMMONIUM CHLORIDE AND POTASSIUM CHLORIDE ON PHOSPHONITRIC NITROPHOSPHATE SLURRY

Amount of KCl added to 600 g. Slurry, g.	Viscosity at 90°C, cp.	Amount of NH ₄ Cl added to 600 g. Slurry, g.	Viscosity at 90°C, cp.
0	225	0	225
5	200	5	200
15	185	15	180
25	160	25	160
35	150	35	130
45	150	45	120
65	145	55	110
85	135	65	100
105	120	85	75
120	110	105	65
		120	60

amount of potassium or ammonium chloride increases; simultaneously there is a corresponding decrease in moisture content also as these chemicals are added in solid state. With ammonium chloride the rate of decrease is more than that with potassium chloride.

Ammonium chloride and potassium chloride themselves have fertilizer value; hence, they can be economically used as viscosity depressants in the production

of N-P and NPK fertilizers through the phosphonitic nitrophosphate route.

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Studies on the Properties of Guanidine Dipicrylamine Complex

By

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Some physical and chemical properties of the complex guanidine dipicrylamine have been studied in this paper. The structural arrangement of the compound reported earlier, has also been discussed in the light of certain chemical reactions.

Introduction

Guanidine salts, like guanidine nitrate, sulphate, carbonate, etc., react quantitatively with the magnesium or calcium salt of dipicrylamine in solution and give a precipitate of guanidine dipicrylamine. This reaction has been utilized for standardizing a method of gravimetric estimation of guanidine¹. It was of interest to study the physical and chemical properties of the compound as the data on such properties are not available in literature.

Properties

The compound is obtained as a chocolate-red needle-shaped monoclinic crystals when a super-saturated solution of it is allowed to cool down slowly. The aqueous solution is orange red in colour. From alcoholic solution the crystals obtained are bigger and prismatic in appearance. The alcoholic solution is deep red in colour, while the colour of the acetone solution is blood red.

Melting point: Its melting point is 243°C as recorded in the Gallenkamp melting point determination apparatus when heated at the rate of 5°C rise per minute.

Explosivity: When 0.5 g. of the compound was heated under a confinement volume of 3 c.c. at the rate of 2°C rise per minute, the explosion temperature on thermal initiation recorded was 254°C. Under similar conditions the explosion temperature of ammonium nitrate recorded was 285°C. These were the temperatures to which the samples were heated just prior to their explosion.

Solubility: (a) IN WATER AT DIFFERENT TEMPERATURES

Temperature, °C	Solubility, g./100 g. water
0	0.0071
20	0.0325
30	0.0430
50	0.0640
80	0.0975

(b) IN DIFFERENT ORGANIC SOLVENTS AT SPECIFIED TEMPERATURES

It is fairly soluble in alcohol and readily soluble in acetone but very sparingly soluble in aromatic hydrocarbon solvents.

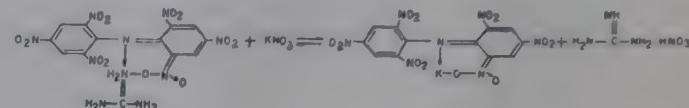
Solvent	Solubility, g./100 g. solvent
Ethyl alcohol	3.1425 at 30°C
Acetone	85.3800 at 30°C
Benzene	very sparingly soluble
Toluene	-do-

Reactions

(a) *With Acids:* It is decomposed easily by inorganic acids, like nitric, hydrochloric, sulphuric and phosphoric acids, to hexanitro-diphenyl amine (dipicrylamine) and the corresponding guanidine salt. Organic acids, like acetic, oxalic and salicylic acids, can also decompose it; citric acid decomposes it with difficulty. The hexanitrodiphenyl amine can be easily filtered out and the

When potassium nitrate solution was added to guanidine dipicrylamine solution in water, potassium dipicrylamine was precipitated out. The table below gives an idea about the extent of reaction of guanidine dipicrylamine with potassium nitrate.

The reaction is a replacement reaction and may be represented according to the following equation.



This exchangability of guanidinium ion by potassium ion is an indirect confirmation of the structural arrangement of guanidine dipicrylamine proposed earlier on the analogy of the potassium dipicrylamine structure.²

The structure (1) given above shows that there is no free lone pair of electrons with the N of -NH in the dipicrylamine part of the complex, as those electrons are already fixed up forming a co-ordinating bond with

*GDPA soln. taken, ml.	Amount of GDPA in the solution, g.	K-nitrate soln. added, ml.	Amount of KNO ₃ in the Solution added, g.	Wt. of KDPA** precipitated out, g.	KDPA Equivalent to GDPA solution added, g	Precipitation percentage of KDPA
100	0.0430	10	0.50	0.0123	0.0412	30
100	0.0400	10	0.60	0.0113	0.0383	29
100	0.0350	10	1.00	0.0100	0.0336	30
100	0.0315	10	0.50	0.0090	0.0302	29
100	0.0355	10	0.50	0.0100	0.0340	29

* GDPA—Guanidine dipicrylamine

** KDPA—Potassium dipicrylamine

filtrate on evaporation gives the guanidine salt. And in this way, guanidine sulphate, chloride, phosphate, oxalate and salicylate were isolated. As dipicrylamine itself is soluble in the acetic acid, isolation of guanidine acetate from the reaction mixture is somewhat difficult[†].

(b) *With Alkali:* The compound is highly soluble in sodium hydroxide solution and less so in ammonia. It is very little soluble in potassium hydroxide solution. Whether the high solubility of the compound in sodium hydroxide is associated with decomposition and its less solubility in ammonium and potassium hydroxide is due to the deposition of their dipicrylamine over it are to be further investigated.

(c) *With Potassium Nitrate:* Potassium ion can substitute guanidinium ion in guanidine dipicrylamine.

[†]A paper on the preparation of guanidine compounds via guanidine dipicrylamine is under preparation.

the electronically deficient nitrogen of the guanidinium ion. It was therefore inferred that guanidine dipicrylamine would not give rise to any derivative when reacted with methyl iodide (CH_3I) or methyl p-toluene sulphonate. Experiments conducted in the line confirmed the inference; no derivative was obtained with methyl iodide or methyl-p-toluene sulphonate.

Acknowledgement

The authors are thankful to Dr. S. Varma, Deputy Superintendent, for providing them the data on the explosion test of the compound.

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Studies on the Scrubbing of Light Oil from Coke Oven Gas by Liquid Absorbents

Part I—Petroleum Wash Oils

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Some petroleum-based wash oils have been studied for their suitability in scrubbing light oil from coke oven gas. Their different characteristics, like desirable specific gravity, low viscosity, high boiling range, high initial boiling point, low emulsification tendency with water, satisfactory light oil absorption capacity, etc., indicate their suitability for the recovery of light oil. Their main drawback is the formation of resinous sludges and choking of the scrubbers, resulting in lower scrubber efficiency. This drawback is reduced when an efficient tar fog removal system is introduced.

In the by-product coke oven plants light oil of the coke oven gas is usually removed by washing the rich gas with a suitable liquid absorbent or by adsorption on solids¹⁻⁶. Among the widely used liquid absorbents, either a coal tar or a petroleum oil fraction is extensively employed⁵⁻⁷. Exhaustive studies on various characteristics essential for a suitable wash oil have already been made¹⁻⁷.

In this paper, some petroleum-based wash oils have been investigated for their suitability in scrubbing light oil from coke oven gas, and their characteristics and efficiencies, as determined in the laboratory as well as during actual use in the gas stream of Sindri factory's coke oven plant, are discussed.

EXPERIMENTAL

Materials Used

The following petroleum-based wash oils were obtained from Messrs Burmah Shell, Calcutta: (i) Wash Oil B; (ii) Wash Oil C and (iii) Solar Oil.

The light oil fraction (crude benzole) was obtained from the coke oven plant at Sindri.

Procedure: (i) *Characteristics of Wash Oils:* For determining the characteristics, like specific gravity, distillation range analysis, viscosity, emulsification with

water, etc., of the above wash oils the appropriate standard methods⁷⁻⁹ were followed (Table 1).

(ii) *Benzole Retention Capacity:* Benzolized wash oils containing varying concentrations of crude benzole (Table 2) were prepared in the laboratory. Dry air was bubbled at 25 c.c./min. through a known amount of benzolized wash oil, of known benzole concentration at atmospheric pressure and temperature ($30^{\circ} \pm 1^{\circ}\text{C}$). For efficient distribution of air a sintered glass bubbler was used. The volume of exit air saturated with benzole vapours and volatile constituents of the wash oil was measured with a wet gas-meter, and the uniformity of the flow was maintained with an orifice-meter. The total amount of benzole and volatile constituents of the wash oil lost was calculated from the difference in weight of the scrubber with contents, before and after passing a definite volume of air through the oil.

Blank determinations were also made for the loss due to volatile constituents of the wash oil only, for the same volume of air passed through the same quantity of wash oil, under exactly identical conditions. The amount of benzole lost from the benzolized wash oil per cubic metre of air passed was calculated by subtracting the blank value from the corresponding total value obtained earlier. The benzole content of the scrubbed air over the benzolized wash oils was calculated and is shown in Fig. 1.

(iii) Sludge Formation in Different Wash Oils: 200 ml. of fresh petroleum wash oil was taken in a gas bubbler, through which 1000 l. of the coke oven gas was passed at 50 l./hr for 20 hours. The benzolized wash oil was then regenerated, and the debenzolized wash oil, thus obtained, was tested for viscosity and finally transferred back into the gas bubbler along with the sludge separated during regeneration. The same procedure of passing coke oven gas, heating for debenzolization, etc. were repeated thrice under the same conditions as described above. After completion of such three cycles, benzole retention capacity and viscosity of the used oil and the total amount of sludge formed were determined (Table 3, Fig. 2.)

TABLE 1—CHARACTERISTICS OF FRESH PETROLEUM WASH OILS

Characteristics	Wash Oil B	Wash Oil C	Solar Oil
1. Specific Gravity at 30°C	0.840	0.893	0.918
2. Viscosity (Redwood No. 1 at 30°C), secs	45	58	51
3. Specific Viscosity (Engler) at 30°C, °E	1.51	2.02	1.82
4. Water Content	Nil	Nil	Nil
5. Benzole Content	Nil	Nil	Nil
6. Distillation Range Analysis	% of Total Oil Distils. Over, by Vol		
Temperature, °C	Wash Oil B	Wash Oil C	Solar Oil
260	—	—	<1
270	<1	—	1.5
280	2	—	3.5
290	7	—	8.5
300	27	<1	18.5
310	49	2.5	33.5
320	65	8.0	50
330	77	21	64.5
340	85	42.5	74.5
350	90	62	82.5
360	94	79	90
370	—	89	93
380	—	94	—
7. Emulsification with Water (100 ml. of the oil shaken vigorously for 30 secs. with 100 ml. of water at 30°C)	About 99% of the oil separated in 10 min.	Oil/Water separation was almost complete in 10 minutes	Oil/Water separation was almost complete in 10 minutes
8. Foam Formation (On aeration at the rate of 25 c.c./min./20 ml. of the oil at 30°C)	Fairly low	Slightly more than Wash oil B	Slightly more than Wash Oil B

TABLE 2—CHARACTERISTICS OF THE LIGHT OIL USED

(a) Specific Gravity at 30°C	0.885
(b) Distillation Range Analysis	
Temperature, °C	% of Total Oil Distils Over, (v/v)
90	48
100	70
110	76
120	80
130	83.5
140	86.5
150	88.5
160	90.5
170	92
180	93.5

(c) Fractional Distillation, % by Vol.

(i) Forerunnings	2
(ii) Benzole	60.4
(iii) Toluol	14.1
(iv) Light Solvent Naphtha	7.5
(v) Heavy Solvent Naphtha	11.0
(vi) Residual Oil	5.0

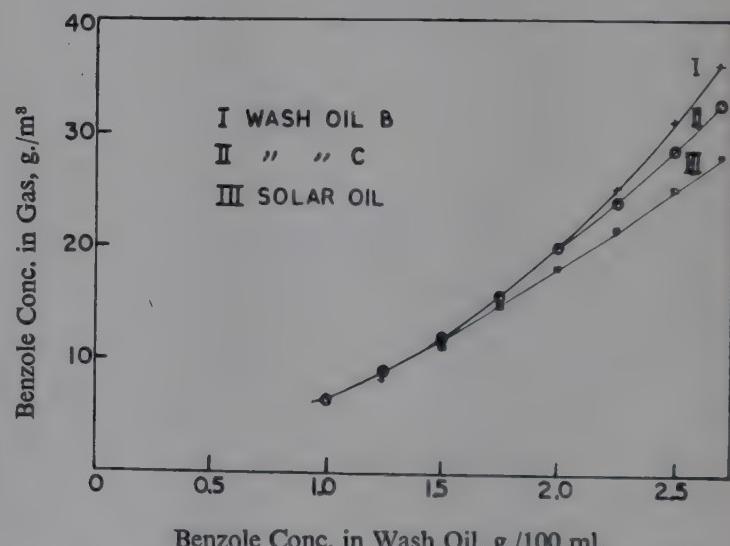


Fig. 1—Variation of Benzole Content in Gas with Change in Benzole Concentration in Benzolized Wash Oils

Results and Discussion

Characteristics: It can be seen that the specific gravity of the oil fractions ranges from 0.840 to 0.918 (Table 1), which is considerably different from that of water. This is desirable for rapid separation of the oils from oil-water

TABLE 3—SLUDGE FORMATION IN DIFFERENT PETROLEUM WASH OILS DURING LIGHT OIL SCRUBBING FROM COKE OVEN GAS

Sl. No.	Cycle No.	Petroleum Wash Oil	Specific Viscosity (Engler) at 30°C, °E	Volume of Oil Taken, ml.	Volume of Coke Oven Gas Passed, l.	Flow Rate of the Gas, l./hr.	Total Amount of Sludge Formed in Three Complete Cycles, g.	Amount of Sludge Formed g./m³ of Coke Oven Gas Passed
I	1.	Fresh Wash Oil B	1.5	200	1000	50	—	—
	2.	Used Wash Oil B (Once regenerated)	—	Whole of the debenzolized oil of cycle No. 1	1000	"	—	—
	3.	Used Wash Oil B (Twice Regenerated)	—	Whole of the debenzolized oil of cycle No. 2	1000	"	—	—
		Used Wash Oil B (Thrice Regenerated)	1.5	—	—	—	0.99	0.33
II	1.	Fresh Wash Oil C	2.0	200	1000	50	—	—
	2.	Used Wash Oil C (Once regenerated)	—	Whole of the debenzolized oil of cycle No. 1	1000	"	—	—
	3.	Used Wash Oil C (Twice Regenerated)	—	Whole of the debenzolized oil of cycle No. 2	1000	"	—	—
		Used Wash Oil C (Thrice Regenerated)	2.0	—	—	—	0.89	0.30
III	1.	Fresh Solar Oil	1.8	200	1000	50	—	—
	2.	Used Solar Oil (Once Regenerated)	—	Whole of the debenzolized oil of cycle No. 1	1000	"	—	—
	3.	Used Solar Oil (Twice Regenerated)	—	Whole of the debenzolized oil of cycle No. 2	1000	"	—	—
		Used Solar Oil (Thrice Regenerated)	1.8	—	—	—	0.80	0.27

admixture and to avoid their emulsification in the decanters. The viscosities are quite low and lie between 45-58 sec. (Redwood No. 1) at 30°C. The oils, being of low viscosity are suitable for better distribution and intimate contact with the gas in the conventional counter-current light oil scrubbers besides having lower pumping costs.

The initial boiling point for all the oil fractions are quite high (260-300°C), and the distillates at 360°C for the wash oils B and C and the solar oil amount to 94, 79 and 90 per cent respectively. As the oils have high initial boiling points far removed from those of light oils, an efficient and complete separation of the light oils from the enriched wash oils, without any chance of introduction of paraffins in the recovered light oil can be achieved. Using these oils, the losses due to vaporization during the scrubbing operation as well as in the debenzolization process would also be considerably low and consequently the requirement of the fresh wash oils for periodical make-up purposes would be lower.

The oils having very slight tendency to emulsify with water, their separation from oil-water mixture was quite rapid and almost complete within the specified period. In case of wash oil B only some foams were found to persist at the oil-water interface, but those were so small in quantity that there was no noticeable difficulty in separation of the major portion of the oil. The observations, made during the course of experiments, indicated clearly that the oil-water separation could be effectively achieved without any danger of emulsification of these oils with water. The foam formed

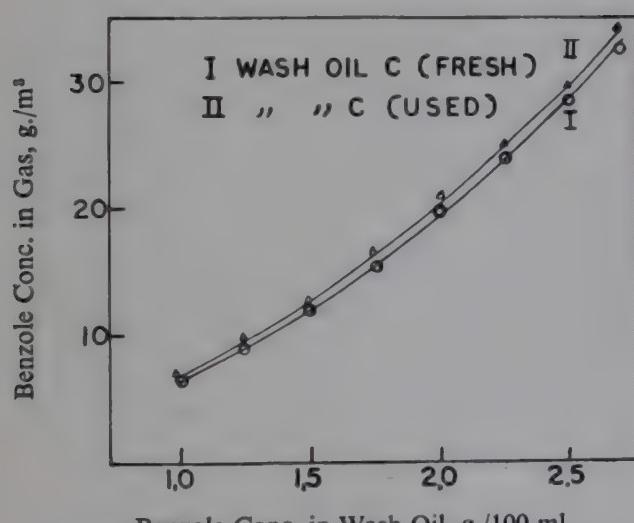


Fig. 2—Change in Benzole Absorption Capacity of Wash Oil on Use under Plant Conditions

during the scrubbing of gas as well as separation of the oils was small; it was minimum with wash oil B. Due to this additional quality, the chances of carryover of the oil with the gas during scrubbing operation are also fairly low.

The low concentrations of benzole in the gas over the benzolized wash oils clearly indicate that upto a benzole concentration of about 2 g./100 ml. of the oil, all the three wash oils have substantially identical benzole retention power, but beyond this concentration solar oil has better retention power, compared to the other two oils (Fig. 1).

Sludge Formation: In the first cycle, on passing 1000 l. of the coke oven gas (outlet gas from the ammonia scrubbers of Sindri factory) through the fresh wash oils, sludge was formed in each case, but it almost completely remained in the suspension state, which made the oils turbid and thick.

In the second and third cycles even on passing only a few litres of the coke oven gas through once- and twice-regenerated used wash oils respectively, the sludge deposition on the surface of the gas bubbler started. The amount of sludge formed increased with the increase in volume of the gas bubbled through the oil and also with the increase in number of regenerations.

During the first regeneration of the benzolized wash oils, colour of the oils became dark, possibly due to the solubility of some of the ingredients of the sludge or tarry compounds, which on heating started separating and depositing on the heating surface of the vessel. This may be due to lower solubility of the sludge in the debenzolized oils, at the temperature of regeneration.

The sludges formed during benzolization and precipitated during regeneration in wash oils B and C were resinous and almost similar in nature, firmly sticking on the surface of the gas bubbler and on regenerating surfaces. However, these could be removed by mechanical means, while the sludge formed with the solar oil was extremely resinous and sticky which was difficult to remove. The determination of total amount of sludge formed in individual oils in the three complete cycles indicated that it is minimum in the solar oil while maximum in the wash oil B. The sludge formed in each wash oil was appreciably soluble in crude benzole, indicating that possibly these consist of high boiling tarry matters, insoluble in the petroleum wash oils.

It is evident from the characteristics of the used

petroleum wash oils that viscosity remains almost unaffected and the benzole absorptive capacity retains almost the same value as that of the fresh oils even after 3 cycles of absorption and regeneration.

Conclusion

The petroleum oil fractions studied, are not only good light oil absorbents but also have high initial boiling points, desirable for effective and efficient debenzolization of the used oils. Moreover, the losses during the regeneration process are also likely to be low resulting in lower requirement of fresh oil.

The viscosity and benzole absorptive capacity of the oil fractions practically remain unchanged during repeated use and hence could be used over again.

The main drawback is the formation of insoluble sludges which are deposited on the surfaces of the scrubbers, heat exchangers and debenzolization equipments. In some cases the sludges formed are extremely sticky and difficult to remove by simple mechanical means. Unless suitable arrangement for their removal is provided in plant, operational difficulties arising from heavy pressure drop and lower scrubber efficiency, etc. may be encountered. The formation of these sludges during light oil scrubbing could be reduced to a considerable extent by purifying the rich gas from tar fog by the use of electrostatic precipitators.

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Deterioration of Jute in Contact with Various Fertilizers

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The extent of swelling and disengagement of individual jute fibres when they are dipped in the saturated solutions of various fertilizers has been determined. Urea solution causes swelling and complete disengagement of the individual fibres constituting the thread whereas with a saturated solution of ammonium sulphate there is no swelling. The swelling and disengagement of individual fibres decrease in the following order: ammonium nitrate > ammonium chloride > di-ammonium phosphate > mono-ammonium phosphate > potassium chloride.

The employment of polythene-lined jute bags do not completely prevent the hygroscopic fertilizer from coming in direct contact with jute. This happens because of the puncture of polythene film during final stitching of the filled bags. During humid season, fertilizer is capable of absorbing moisture through the stitch holes and the moist fertilizer, i.e. saturated solution of the fertilizer comes in direct contact with jute. A glaring instance is that of urea which due to its strong interaction with jute not only wets the mouth of the jute bag but eventually the bag as a whole becomes damp with a decrease in its mechanical strength.

This observation leads to our earlier communication¹ on the wettability of jute fibres in which it has been shown that wetting characteristics varied from fertilizer to fertilizer. A saturated solution of urea wets the jute almost instantaneously, whereas ammonium sulphate does not. Apart from these two extreme cases, only generalized conclusions could be drawn from the results about wetting characteristics of other fertilizers because of the complicating factors, such as the moisture content of jute, density of saturated solutions, etc. It is obvious that these factors would affect the sinking time of the jute test pieces in Seyforth and Margan test². It has been shown that swelling occurs when jute fibres come in contact with water or salt solutions. This affects the mechanical strength of the fibres. Little is known, however, of swelling of the jute fibres in a fertilizer solutions.

The reduction of mechanical strength of jute is related to the weakening of the individual threads constituting the jute or hessian cloth. Two factors come into play: the disengagement of individual fibres constituting the thread and the swelling of fibres. Both these factors are taken into account when we measure the transverse swelling of jute thread. In this communication, the extent of overall swelling of thread of jute has been determined for various fertilizers.

The complex nature of the structure of jute fibres has been emphasised by several workers³⁻⁶. The presence of hydrophylic groups in the large exposed surface causes jute to absorb water. The swelling behaviour of jute fibres in water and dilute solutions of acids and alkalis have been studied by a number of workers⁷⁻¹⁰. Herman¹¹ pointed out that in highly oriented cellulosic fibres, the axial swelling was much less than transverse swelling. A similar behaviour was observed in the case of jute fibres. In the present work the test piece comprising single thread of jute was taken each time and immersed in a saturated solution of fertilizer in a petri dish. The increase in diameter of the thread was measured with the help of a cathadometer fitted in a travelling microscope. The removal of saturated solution before measuring did not give reproducible results on account of squeezing effect. Therefore, measurements were carried out with a piece of jute thread dipped in a fertilizer solution and the percentage increase in diameter was noted (Table 1).

TABLE I

Saturated Solution of Fertilizer	Swelling, % (Average of six determinations)
Ammonium nitrate	300
Ammonium chloride	140
Urea	Complete disengagement of fibres
Mono-ammonium phosphate	90
Diammonium phosphate	110
Superphosphate (Powder)	Complete disengagement of fibres
Superphosphate ammoniated-granular	140
Ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ + Superphos + KCl (2-1-1)	No swelling or disengagement
$(\text{NH}_4)_2\text{SO}_4$ + Superphos + KCl (1-1-1)	50
	140

% Swelling in distilled water—220

Results

The results are fairly reproducible and each value recorded is an average of six determinations. The observed swelling measures the combined effect of the transverse swelling as well as the disengagement of individual fibres in threads. The disengagement of the individual fibres in threads probably occurs due to the increased interaction between the solution and the jute fibres overcoming the cohesive forces which keep the fibres together.

The extent of disengagement and swelling varies from fertilizer to fertilizer as shown in the results. The jute thread has been found to swell to the extent of 200 per cent in distilled water. The extent of swelling in a saturated solution of fertilizer in one of the cases, viz. ammonium nitrate was slightly more than that of water. The measurements with urea solution could not be made

because the fibres swelled and were immediately completely disengaged. Similar behaviour was noticed with powdered superphosphate. Test pieces remained intact in case of a granular ammoniated superphosphate.

Complete disengagement of jute fibres coming in contact with the saturated solution of powdered superphosphate was probably due to the free phosphoric acid normally present in the product. The fibres undergo rapid deterioration on coming in direct contact with free phosphoric acid.

No swelling was observed in the case of ammonium sulphate. The extent of swelling in NPK (2-1-1) was considerably less than in the product (1-1-1). Both these samples were made by granulating together ammonium sulphate, superphosphate and potassium chloride. Since the amount of ammonium sulphate is more in 2-1-1 product, the inhibiting influence of sulphate ion is more pronounced. Swelling was relatively more in di-ammonium phosphate than in case of mono-ammonium phosphate.

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Unit Cell and Space-Group for Methylene Diurea

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Methylene diurea, $(\text{NH}_2\text{CONH})_2 \text{CH}_2$, has been obtained as cold water-soluble portion of urea-form fertilizer and its unit cell dimensions and space-group have been determined. It belongs to orthorhombic system having $a_0=7.235$, $b_0=8.87$ and $c_0=9.62 \text{ \AA}$ with space-group P 222₁.

In an earlier communication¹ it was reported that dimethylene triurea has been found to be the cold water insoluble portion of the urea-form fertilizer prepared with molecular ratios of urea to formaldehyde (U/F) 1.5:1 to 2.0:1 at pH-4 and at room temperature. When the cold water-soluble portions of these compounds were examined for their crystalline phase composition, it was found that they contained an unidentified phase along with varying amounts of free urea depending upon the molecular ratio of the reactants. An attempt was, therefore, made to obtain separately the unidentified phase and to determine its unit cell parameters and space-group.

When the cold water-soluble portion was crystallized by slow evaporation of water at room temperature no good crystals could be obtained. When this ill-crystallized mass was dissolved in methanol and recrystallized at room temperature, crystalline hard spherical lumps of diameter below 0.5 mm. along with needle-shaped urea single crystals were obtained. One of these spherical lumps, used as a single crystal in a rotation x-ray camera, gave a diffraction photograph of finely powdered crystals showing that the spherical lump consists of crystallites of a well crystallized new compound. Such lumps were separately picked out to obtain a powder diffraction pattern in a Guinier camera and for density measurements.

For indexing the powder lines and to determine the unit cell parameters the reciprocal lattice method was followed² as in the case of dimethylene triurea. The

$\frac{1}{d_{hkl}^2}$ or Q_{hkl} values were obtained for all powder lines and the differences, i.e., ΔQ 's for all observed Q_{hkl} values were tabulated (Table 1), from which it was found that the values 0.0193, 0.0129, 0.0108 and their multiples by 4, 9, 16 etc. occur many times. Therefore, any one of these values or their combinations were assumed to be the unit cell parameters for the reciprocal lattices, and Q_{hkl} values for different reflections corresponding to isometric, tetragonal or hexagonal systems were calculated. When no satisfactory agreements between the observed and calculated Q_{hkl} values for the above systems were obtained, these ΔQ values were tried for an orthorhombic system. This time the agreement was found to be satisfactory. A further refinement of these values yielded 0.0191, 0.0108 and 0.0127 to be the parameters for the reciprocal lattice cell. The comparison of observed and calculated Q_{hkl} values are shown in Table 1. The unit cell dimensions calculated assuming the above values as final were $a_0=7.235$, $b_0=8.87$ and $c_0=9.62 \text{ \AA}$.

In an attempt to determine the space group, a survey for systematic absences for reflections were made. It was found that among the reflections of the type 001, 1 odd were absent. No other systematic absences were observed. Therefore, the space-group for this compound was fixed to be P 222₁ in the orthorhombic system.

In order to determine the molecular weight a density determination for this compound was made, using a flotation method in a liquid mixture of carbon disulphide

TABLE I—X-RAY DATA OF COLD WATER-SOLUBLE PRODUCT

Sl. No.	Int.	d (Å)	Q _{hkl} obs.	Q _{hkl} Calc.	Difference	hkl
1.	w	6.48	0238	0244	+0006	200
	vvw	4.81	0432	0432	0000	020
2.	vvw	4.70	0453	0453	0000	002
3.	vvw	4.64	0465	0465	0000	211
4.	vw	4.40	0516	0513	-0003	201
5.	tr	4.32	0536	0545	+0009	013
				0549	+0013	300
6.	vw	4.08	0601	0606	+0005	121
7.	s	3.98	0631	0621	-0010	112
8.	vvw	3.795	0694	0696	+0002	202
9.	mw	3.60	0772	0770	-0002	311
10.	vvw	3.475	0828	0804	-0024	212
11.	vvw	3.301	0918	0894	-0014	022
12.	mw	3.205	0974	0972	-0002	030
13.	mw			0976	+0002	400
14.	mw	3.193	0980	0981	+0001	320
15.	vw	3.160	1001	1001	0000	302
16.	m	3.020	1096	1089	-0007	321
				1094	-0002	402
17.	vvw	2.886	1201	1197	-0004	411
18.	vvw	2.81	1266	1261	-0005	203
19.	vvw	2.575	1508	1510	+0002	123
20.	vw	2.52	1575	1566	-0009	303
21.	vvw	2.50	1600	1625	+0025	500
22.	vvw	2.46	1652	1668	+0016	232
				1674	+0022	313
23.	vw	2.412	1719	1728	+0009	040
24.	vvw	2.348	1814	1804	-0010	004
25.	vvw	2.220	2029	2052	+0023	204
26.	vvw	2.180	2104	2101	-0003	413
27.	vw	2.160	2143	2160	+0017	214
28.	tr	2.130	2204	2196	-0008	600
29.	vvw	2.020	2451	2465	+0014	314
30.	vw	1.990	2525	2509	-0016	522
31.	vw	1.835	2970	2989	+0019	700
				2989	+0019	243
32.	tr	1.710	3420	3430	+0010	504
33.	tr	1.665	3607	3614	+0007	533
34.	vvw	1.559	4114	4114	+0000	713
				4112	-0002	614
35.	vvw	1.515	4357	4336	-0021	820
36.	vvw	1.505	4415	4401	-0014	162
				4405	-0014	534
37.	vvw	1.328	5670	5689	+0019	750
38.	tr	1.265	6249	6268	+0021	470
39.	tr	1.175	7243	7232	-0011	008
40.	tr	1.150	7561	7584	+0023	218
41.	tr	1.125	7901	7888	-0023	408

s—strong.

w—weak.

m—medium.

vw—very weak.

tr—trace.

mw—medium weak.

vvv—very very weak.

and carbon tetrachloride. The average density of a few measurements was found to be 1.43. Making use of the determined unit cell parameters and the observed density, the molecular weight of the compound came to be 528.

The condensation products of urea and formaldehyde under acidic conditions are normally polymethylene ureas³⁻⁵ and free urea. In view of this when the molecular weight for methylene diurea was calculated for four molecules it came to be 528 which is exactly the same for the cold water-soluble unidentified portion of the urea-form fertilizer.

Thus, the cold water-soluble portion of the urea-form fertilizer prepared with molecular ratios U/F 1.5:1 to 2.0:1 at pH-4 and at room temperature is identified to be methylene diurea and free urea. It is determined that

methylene diurea belongs to the space-group P 222₁ in the orthorhombic system having $a_0=7.325$, $b_0=8.87$ and $c_0=9.62$ Å with four molecules per unit cell.

Further work to obtain single crystals to confirm the above findings and to determine the structure of methylene diurea is in progress.

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Indirect Estimation of Phosphorus in Rock Phosphate by Atomic Absorption Spectrophotometer Using Ion-Exchange Decomposition Technique

By

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Phosphorus has been estimated by employing its depressing effect on calcium absorption. The samples were prepared by shaking the powdered rock phosphate with cation-exchange resin and water. The ion-exchange decomposition technique was found ideal for the estimation of phosphorus by atomic absorption spectrophotometer (AAS), because it eliminates the interfering anions which are added in the acid digestion technique and thus saves one step. The results are in good agreement with those of the chemically analysed samples.

It has been reported earlier¹ that the phosphorus can be estimated indirectly by atomic absorption spectrophotometer by passing the acid-digested sample through the cation-exchange resin using the depression of phosphorus on strontium. In the acid digestion process anions other than phosphorus were added in the sample which interfere in the analysis but the interference was minimized by suitable sample preparation.

In the present investigation instead of acid digestion, samples were decomposed by cation-exchange resin directly as was done by Schafer². The powdered rock samples were shaken with cation-exchange resin—sufficient to exchange all cation—and water at 80°C for 2 hours as suggested by Schafer. The cations were adsorbed by the resin and the solution contained all the phosphorus as phosphoric acid. In this solution,

hydrofluoric acid was also present as the rock samples contain generally high fluorine. Schafer found that ion-exchange decomposition is very much suitable for the simultaneous determination of phosphorus and fluorine. In the case of rock phosphate 2 hours' shaking recovers completely the phosphorus and fluorine in the solution. But in case of aluminium phosphate complete recovery of phosphorus requires about 16 hours' shaking. In the present work only rock phosphate has been studied.

Effect of Fluorine

Since fluorine present in the rock phosphate is about 4 per cent, it was considered necessary to see its effect on calcium absorption. Adams³ et al have observed that fluorine does affect the barium absorption considerably in total consumption burner, but not in the premix burner. The effect of fluorine on calcium in the Perkin Elmer Premix burner using air-acetylene flame is shown in Fig. 1. It was observed that at low concentration there is no effect of fluorine on calcium but a high concentration depresses the calcium absorption. At 0.01 N fluoride solution, the recovery of calcium was about 98 per cent. Since fluorine was less than 1 ppm in the final working sample, no interference was expected in the analysis.

Sample Preparation

50 mg. of finely powdered sample was taken in a polythene bottle and shaken with about 10 g. of Amberlite IR-120 (H^+) and 30 ml. of water at 80°C. The shaking was done on a mechanical shaker for 2-3 hours and then filtered. All the working samples and standards were prepared having 10 ppm calcium. Standards containing 0-5 ppm of phosphorus were prepared, by adding various amounts of 200 ppm of phosphorus solution, obtained by passing the di-sodium phosphate solution through cation-exchange resin. In the working samples, phosphorus concentration was brought down to 1-4 ppm by suitable dilution prior to the addition of calcium.

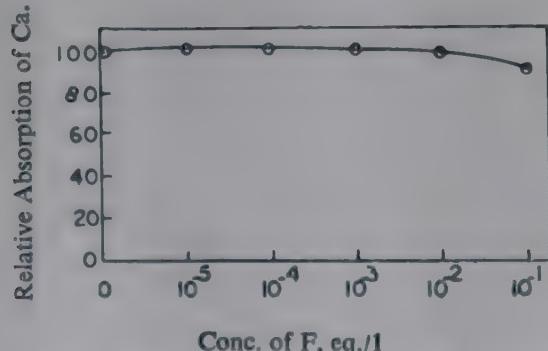


Fig. 1—Effect of Fluorine on 10 ppm Calcium

Experimental and Results

Perkin Elmer 303 model atomic absorption spectrophotometer equipped with air-acetylene premix burner and digital readout accessory (DCR-1) were used. The hollow cathode lamp of calcium was also of Perkin Elmer make. The burner height was kept 1.25 while the other analytical conditions followed were the same as given in the standard methods⁴. DCR-1 was adjusted and an average of eight values was taken.

The calibration curve was drawn between the absorption of 10 ppm calcium and phosphorus concentration (Fig. 2). The results are given in the Table 1.

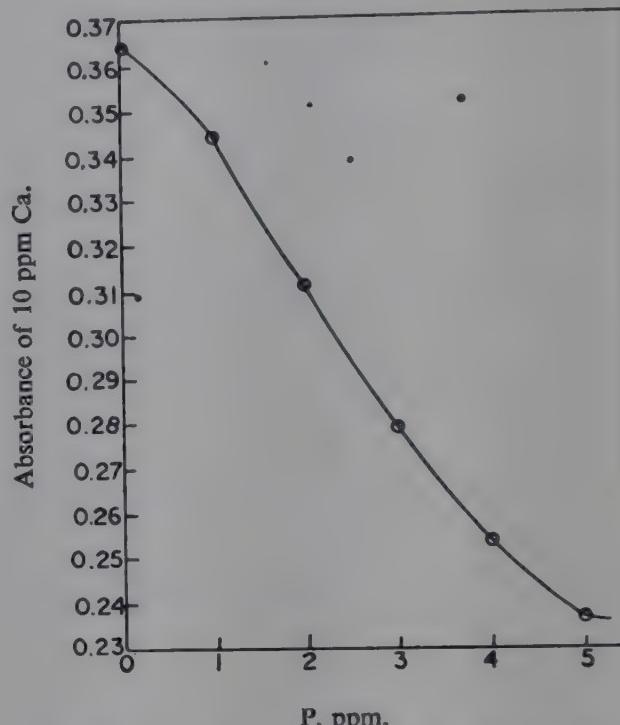


Fig. 2—Calibration Curve for Phosphorus

TABLE 1

Sl. No.	P_2O_5 by Ion-Exchange Decomposition (AAS), %	P_2O_5 by Acid Digestion (Chemical Analysis), %	Deviation
1	41.68	41.50	+0.18
2	40.82	40.26	+0.56
3	38.24	39.02	-0.78
4	40.25	42.15	-1.90
5	34.45	33.58	+0.87
6	35.49	35.92	-0.43
7	9.59	9.50	+0.09
8	27.30	28.05*	-0.75
9	25.19	25.30*	-0.11
10	28.06	28.45*	-0.39

*Analysed by AAS using acid digestion¹.

Discussion

It is evident that the results obtained by the ion-exchange decomposition technique are in good agreement with those by the chemical analysis (Table 1). The method is superior to the acid digestion method used earlier¹ as it eliminates the effect of anions which are added in the digestion process. This method can be utilized for the estimation of phosphate in rocks, but in case of aluminium phosphate sixteen hours shaking is required as suggested by Schafer². The added advantage of the ion-exchange decomposition method is that fluorine can be chemically analysed in the filtrate free from the cationic interferences. Calcium can also be estimated by AAS by eluting calcium ions from the ion-

exchange resin, eliminating the interference of phosphorus and other interfering ions. This method does not require any attention during shaking. It is simple and comparatively quick when bulk samples are to be analysed and can be compared with the chemical methods in accuracy.

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Hydrodesulphurization of Petroleum Feedstock Using Alkalized Iron Oxide Catalyst —A New Process

The rapid growth of industries based on petroleum feedstock has necessitated the availability of relatively sulphur-free products for further processing. Such feedstocks are always associated with different types of organic sulphur compounds, like carbon disulphide, mercaptan and thiophene, etc., in varying quantities. In the dry purification processes for hydrodesulphurization in commercial operations cobalt-molybdate is being most commonly used. The ingredients of this catalyst are, however, not indigenously available and hence an attempt has been made to develop an alternative hydrodesulphurization catalyst based on indigenous raw materials.

Such a catalyst may be an alkalized iron oxide, which has been used in Germany¹ for removal of organic sulphur compounds from synthesis gas by oxidation in presence of air. However, the available information regarding its use is insufficient².

Studies so far carried out in this Division are very encouraging and indicate that an alkalized iron oxide catalyst of a suitable composition can be used for removal of carbon disulphide and mercaptan types of sulphur compounds; however, it is completely unsuitable for removal of the thiophenic type. The latter may, however, be easily removed by acid treatment, and for that purpose an activated acid treatment process has also been developed.

The spent alkalized iron oxide catalyst may be regenerated easily by simply steaming at elevated temperatures and reused (Fig. 1).

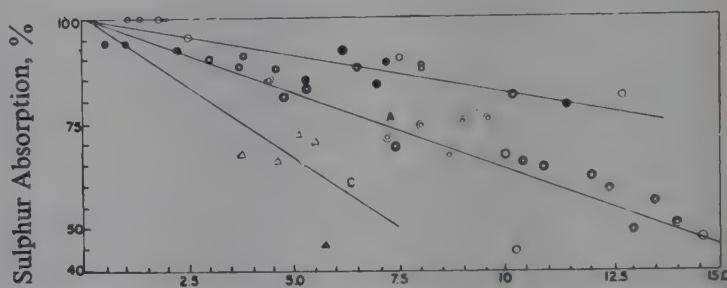
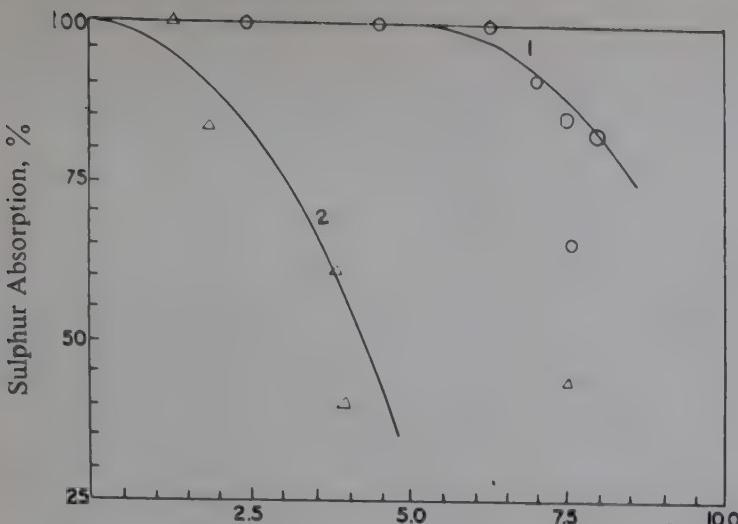


Fig. 1—Retention vs. Percent Sulphur Absorption with Carbon Disulphide

Legend

- A. 50 g. Catalyst Containing 5% alkali. Feed-heptane soln. containing 350-500 ppm 70-110 cc. liq./H₂, hydrogen rate 7-10 l./hr. Temp. —300°C, pressure—atmospheric
- B. Same as A after regeneration with steam at 400°C
- C. 50 g. catalyst containing 15% alkali Feed—heptane solution containing 1400-2000 ppm. CS₂ 48-60 cc. liq./H₂. hydrogen rate 9-14 l./hr. Temp. —300°C, pressure—atmospheric

From the limited data available, it appears that for removal of carbon disulphide an alkalized iron oxide catalyst of a low alkali content is preferable, whereas



Retention of Sulphur, g./100g. cat.

Fig. 2—Retention vs. Percent Sulphur Absorbent with Mercaptan

Legend

1. 50 g. catalyst containing 20% alkali Feed—heptane soln. containing 800-1200 ppm. mercaptan; 80-100 cc liquid/hr., hydrogen rate 11-13 l./hr. Temp.—300°C; pressure—atmospheric
2. 50 g. catalyst containing 15% alkali Feed—heptane soln. containing 600-3000 ppm. mercaptan; 42-66 cc. liquid/hr, hydrogen rate 11-14 l./hr, Temp. —300°C; pressure—atmospheric

for removal of mercaptan sulphur higher alkali content is preferred (Figs. 1 and 2).

Hydrodesulphurization with alkalinized iron oxide catalyst together with prior acid refining may be a suitable substitute for hydrosulphurization with cobalt molybdate and zinc oxide catalysts as used in the pretreatment of naphtha in the ICI's steam-reforming process.

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Notes & News

Large Ammonia Plant

The current trend in ammonia plant is in favour of large capacity single-train units in which reforming is carried out at a higher pressure and the ultimate ammonia synthesis at a lower pressure. The production of synthesis gas at pressures of 500 psi results in mechanical equipment design and catalysts problems. For large single-train capacities very large converters are needed which work at lower pressures, 2000-3000 psi, to accommodate the use of centrifugal compressors. Some problems from the view points of operation and fabrication are discussed here.

Operation: Centrifugal compressors are used almost throughout, although some designs favour turbine-driven reciprocating compressors for flexibility using the steam produced in the high pressure boilers in the reforming section, thus economizing considerably on manufacturing costs. In many designs the steam from the turbine discharge is used as reformer feedstock; thus the boiler feed water must be purified, otherwise silica and other impurities will form scale in the heat exchangers. Silica migration occurs mainly from the secondary reformer and it can foul sensitive waste-heat boilers and shift converter catalyst. Other contaminants in waste heat boilers include Fe_2O_3 , Al_2O_3 , MgO , CaO and P_2O_5 .

The primary reforming catalyst can be completely ruined by a rapid increase and decrease in pressure. In natural gas based ammonia plants (working pressure 500 psi) the degree of sulphur removal must be high to maintain the efficiency of the reformer catalysts. Where the final desulphurization catalysts are of acidic, anionic-promoted activated carbon type, corrosion due to the acidity of condensate has been reported. When the plant is in full operation, high pressure steam generated in the secondary reformer often accounts for something like 75 per cent of turbine driven power. Although catalysts sometimes give rise to problems, operational difficulties that arise are usually mechanical in nature.

Fabrication: A notable part of the difficulties in operation and start-up may be attributed to faults in equipment and components. In a recent paper by G. P. Eschenbrenner et al one major problem of fabrication pointed out was the inability to obtain the required physical strength conventional heat treatment with large low-chrome alloy steel converters, due to the size and weight of the vessel courses. It was found that the physical strength from hardness test did not attain the required value after tempering and the steel had properties of resembling annealed steel, the reasons for this were firstly because of the large mass of steel and the size of the courses and, secondly that the furnace used for normalizing was too far from the rolls where quenching was conducted so that still-air cooling takes place in the meanwhile. Satisfactory results were obtained by (i) heating of courses to 940°C , (ii) immediate water-cooling both inside and outside, while the course is rerolled; (iii) tempering at $660-680^\circ\text{C}$, (iv) intermediate and final stress relieving at $530-610^\circ$ and 670°C respectively. A second problem was encountered during the hydrostatic test when strain gauges indicated axial and circumferential strain in some vessels.

Electroslag welding is commonly used followed by thorough non-destructive testing of each weld. An experienced fabricator ran into serious defects with his eight converter (of steel 24 Cr, Mo 10), the defects comprising herring-bone line of shrinkage cracks along the axis of the weld and a longitudinal fault along the fusion zone.

In three shift converters, each for a 1000 tpd. ammonia plant, trouble arose with attachment of 18 inch nozzle with a stub end for field welding to an external pipe. The cracking was overcome by applying a weld deposit to the forging by submerged arc technique.

Economic Advantages: Among the advantages of large single-train ammonia plants are (i) with increase in capacity, the direct labour cost per unit of production de-

creases and the initial plant cost increases at a rate lower than the corresponding increase in capacity, (ii) increased capacity allows a change in the equipment used.

The sizes of the heat exchangers are however limited, although the actual limits depend upon the type of exchanger in question. The shell and tube types are limited by their diameter. Normally in the large plants, heat transfer is effected with multiple units and with increased capacity the cost would tend to rise at a slightly less than linear rate.

Pumps are limited by the hydraulics of the piping system and their net pump suction head requirement; sometimes boosters are necessary. Centrifugal and axial compressors are available with hundreds of thousand CFM and discharge pressure upto 5000 psi. Multiple case compression is limited by the power of the driver. Motors are generally limited to 10,000 h.p. Gas turbines, generally available to 30,000 h.p., can be increased to 50-100,000 h.p. using jet engine gasifier feed. Limits on the horse power of steam turbines are very high. Machinery costs tend to increase at a slightly less than linear rate with increased capacity. Pipe diameters increase in proportion to the square root of the capacity and pipe thickness increases linearly with diameter, thus the weight per foot of pipe increases linearly with capacity. However, the piping costs for larger pipes increase at a greater than linear rate, while instrumentation, foundations and steelwork costs tend to increase at a lower than linear rate. Thus, it can be seen that plant investment costs will increase roughly linearly with plant capacity and so economical advantages of such plants will depend on chiefly technological improvements in process design materials, fabrication and construction.

[*Nitrogen*, No. 51, (1968), 21]

Progress in Urea

Modern technology is changing so fast that new modification over existing process for economic and better yield has become

a common feature. When the product is in greater demand the changes are prominent. The improvements in the fertilizer technology are conspicuous as the worldwide demand for fertilizer is growing. Amongst the various fertilizers the use of urea is increasing day by day and to cope up with this growing demand bigger capacity urea plant is inevitable. Last two decades have witnessed the rapid and fast technological changes in urea manufacturing process aimed at profitable yields. The efforts were made wherever possible to eliminate any stages in manufacture and better utilization of energies like steam, electricity.

The main advantage of Toyo Koatsu's *Ammo-Urea* process is the elimination of CO_2 removal stage after the synthesis gas has been made. The process uses the raw synthesis gas e.g. from steam-reformed naphtha containing a large proportion of CO_2 . By compressing the synthesis gas to 300 atm and reacting with NH_3 in an absorber, carbamate is formed. This is then pumped to a second reactor where the pressure is reduced to 250 atm causing degassing of the synthesis gas which is practically free of CO_2 and NH_3 and can be used for ammonia synthesis. In *Chemico's Thermo-Urea* process, the off-gases are compressed centrifugally at a temperature above carbamate decomposition. Capital cost for a plant of this type is lower than a plant using solution recycle, and the thermal equivalent to the extra power consumed in adiabatic compression is partly recovered as steam, and partly used for preheating feedstock.

A process developed by Snam Progetti is carried out at 100-150 atm using a NH_3/CO_2 ratio of 3.5:1. Carbamate formed is decomposed to urea at the same pressure, ammonia being used as stripping medium. The process can be carried out at higher temperature without corrosion and formation of biuret which usually occurs during carbamate decomposition. It is claimed that 0.8 ton of steam is consumed for each ton of urea produced. This improvement reduces the steam requirement to half—as in other processes an average of 1.6 ton of steam per ton of urea produced is used. Further, the energy required is 150 kWh/ton urea compared with 170 kWh/ton for other processes.

[*Chem. & Proc. Engng.*, 49 (3) (1968), 3]

Stabilizing Ammonium Nitrate Against Crystalline Change Caking and physical breakdown of

ammonium nitrate prills and granules to dust or fine particles in storage have caused troubles to both producer and user as they experience serious product deterioration. Numerous patented processes have sought to overcome this problem. Potassium nitrate, magnesium nitrate and nucleating agents, like silicates, clay, talc and naturally occurring silica materials, are being used commercially but with no use. Instead of solving the problem they are found to create more complications e.g. magnesium nitrate increases the resistance of ammonium nitrate to breakage at the transition points, it increases the hygroscopicity and the prills are subjected to "sugaring", a breakdown of prills to fine particles resembling sugar granules. It also causes a change in crystal structure as moisture is either absorbed or migrated in potassium nitrate and nucleating additives give only limited resistance to transition breakage.

A new most effective method for stabilizing ammonium nitrate against physical breakdown is patented by Brown M. L., et al in U.S. Patent 3,317,276 (May 2, 1967). Ammonium nitrate prills produced by this patented process retain their hardness and are much harder with high resistance to breakage by physical shock; extremely stable to transition temperature breakdown; not subjected to sugaring; less hygroscopic than ammonium nitrate without additives or both previously reported additives; and much more resisting to caking. Production cost can be decreased by \$0.3 to 2 per ton, depending upon particular plant. In addition, the savings resulting from reduced buyer complaints and reduced reprocessing of returned or stored product and reduced bag breakages have been realised.

By adding less than 0.5 per cent of a mixture of boric acid, DAP (diammonium phosphate) and ammonium sulphate to ammonium nitrate melt prior to prilling or granulating, an extremely stable product can be produced. Fines and dust production in both high and low density plants is reduced sharply. Prills completely stable to over 1400 cycles of 90°F, transitions are produced.

The mixture of H_3BO_3 , $(\text{NH}_4)_2\text{PO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ is prepared as solution and fed into ammonium nitrate melt ahead of the prilling tower by a proportioning pump. As the solution has a low viscosity and dissolves in ammonium nitrate, pumping is no problem and spray heads do not plug. After 9 months of continuous use in a

low density plant and test runs in a high density plant indicate the following advantages.

To prevent excessive formation of dust and cracked prills, the prill temperature at the bottom of the prilling tower is generally maintained between 165 to 178°F. Use of this additive permits temperature from 160 to 200°F and formation of fines is greatly reduced. The dust emission from the tower can also be reduced by reducing air velocity through tower. There is impressive steam saving and less equipment cleaning is required. Plant capacity is increased by 10 per cent.

After two years of storage, low density product is in excellent condition after more than 300 transitions. Although some of the products contain 0.6 to 0.8 per cent moisture no caking has occurred. In the high density plant, the amount fines leaving the prilling tower and the cooler is reduced to about 30 per cent of that present without additives. High density prills with hardness index of 80 or higher resulted and the prills retain their hardness with aging. Clay and diatomaceous earth adherence is improved as 2.5 per cent can be uniformly applied to high density prills. A 10-fold improvement in storage stability is observed in an ammonium nitrate-ammonium phosphate mixed fertilizer.

[*J. Agr. Food Chem.*, 16 (3) (1968) 373]

Controlled Release Fertilizers

The slow-releasing fertilizers are made to control the rate of releasing the plant materials or nutrients into the soils. There is presently a modest use of controlled release fertilizers on high cash crops and in the non-farm market. Ureaform (introduced commercially in 1955) has value as a nitrogen fertilizer for turf grass and ornamental plants which need a prolonged supply of nitrogen for optimum growth. MagAmp, magnesium ammonium phosphate ($\text{Mg NH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), is a long-lasting non-leaching, non-burning slow-release fertilizer with an analysis of 7-40-6. Osmocote, is another polymeric coated slow release fertilizer. It consists of granules or prills of soluble nutrients enclosed in a water permeable resinous film. The coating accounts for 10-15 per cent of the weight of the material. Thickness and chemical composition of the coating film determine leach rate.

Thiokol Chemical Corpr. has just developed a low cost slow-release fertilizer coating which consists of a thin coating of flexibilized sulphur and a method of applying it to several types and shapes of fertilizer. Coating costs range about \$10 per ton of fertilizer. Smooth urea prills coated by this process would be priced as low as \$110 per ton compared to other slow-releasing fertilizers such as urea-form and MagAmp currently selling at \$260 and \$400 per ton. In the Thiokol process satisfactory coatings of spherodized urea can be achieved with a sulphur coating which is 10 per cent by weight or less of the finished product. The coating is hard and material is free-flowing, dust free and has shown no tendency to cake.

Action of the soil micro-organisms gradually breaks down the sulphur coating, thereby releasing valuable sulphate ions. Thus, the coating has additional advantage of supplying sulphur in sulphur deficient soils.

The potential advantages of this slow-release fertilizers include greater efficiency of use through reduced leaching losses in irrigation or high rainfall areas; less hazard of injury from high rates of application; lower labour costs because of reduced frequency of application; better growth due to continuous supply of nutrients and fertilizer application can be scheduled whenever it is convenient.

[*Farm Chemicals*, 131 (5)
(1968), 18]

Girdler Single-Tank Reactor for Phosphoric Acid

For the reaction system in a wet process phosphoric acid plant, research by C & I Girdler indicated that the simplicity and potential savings of the single reactor system appeared to offer substantial improvements in wet process technology. About five tons of gypsum is produced per ton of P_2O_5 in the wet process manufacturing of phosphoric acid and the objective of the process would be to produce suitable calcium sulphate crystals to be separated from liquid phase with speed and efficiency.

Factors influencing efficient crystal formation and extraction are dependent on (1) the method and rate of addition of the reactants, (2) the dispersion of the reactants in the reaction mass, (3) sulphate in distribution in the reaction mass, (4) reaction temperature and (5) the time available for the completion of the

reaction and crystal growth. The characteristics of the rock phosphate, the strength of the sulphuric acid used and the phosphoric acid produced influence any of the above factors.

A careful analysis of the design features influencing these factors led to a single tank reactor being designed, which satisfy most of the needs for growing crystals. The initial small-scale pilot plant reactor was a rectangular polygon with a longitudinal partition, which could be considered as a continuous rectangular trough with no partitions or compartments which has been folded over in the middle, thus bringing both ends of the trough back together and closing the circuit around the inner wall. A series of agitators keeps the slurry circulating at a rate estimated to be 10 times higher than could be obtained by using pumps for external circulation; thus, the sulphate ion and temperature gradients throughout the system could be reduced to negligible values.

The results obtained from the initial pilot plant studies were sufficiently promising to convince C & I Girdler that no large-scale pilot plant work would be needed, and work could confidently proceed to the design of the first full-scale unit. A plant based on this process has been built at Calgary, Alta.

The tank shell was constructed from reinforced concrete, as was the reactor cover which was keyed to the walls. A sprayed, natural rubber membrane was applied to the bottom and the walls of the vessel, the underside of the cover being sprayed with PVC, and an anti-corrosive mastic layer being applied to the top. A layer of carbon brick was used on the walls and bottom, with an additional insulating layer of acid brick between the carbon and the rubber membrane on the bottom. Special provisions were made in the design of the concrete shell to ensure the stability of the carbon brick wall lining after application.

Special care was given to the design and specification of the agitation mechanism, since this was one of the requirements laid down in the original design study. Six units, with a total rating of 400 h.p., are used, with totally welded impellers so as to minimize corrosion and wear on bolts holding the turbine agitator blades. 317L stainless steel is used for the impellers, for maximum corrosion resistance when Western phosphate ores are used, with special provisions for added protection of the shaft at the

vapour-liquid interface. The agitator drives are standard Mixco units, with hollow quill gear reducers, equipped with special couplings for protection against shocks. The mounting of the agitators is such that all of them can easily be repositioned in plan in any of four different positions, so as to modify or improve patterns of agitation inside the reactor. In addition, all the impellers can be adjusted vertically.

Sulphuric acid can be added at either 93 per cent concentration or diluted in an external Karbase cooler down to 70 or 55 per cent H_2SO_4 . The results of the plant were satisfactory.

[*Phosphorus and Potassium*, No. 33
(1968), 31]

Effectiveness of Different Fertilizers Used by the Developing Countries

The FAO Fertilizer Programme, organized under the auspices of the Freedom from Hunger Campaign, has become a highly successful project in the developing countries which are receiving fertilizers. Crop yields of these countries where fertilizers along with other improved practices have been used have increased at least 50 per cent. Among the fertilizers nitrogenous fertilizers have been effective and profitable everywhere, except under semi-arid conditions (annual rainfall below about 350 mm.). Soluble phosphate has also proved of value and profitable almost everywhere, including low-rainfall areas. Potash was frequently effective and profitable, but there were also cases where potash produced little or no response. In just over half the simple trials, a single or double nutrient treatment was equally or more effective than a complete NPK treatment, and in just half the trials the complete NPK treatment gave a higher yield than any single nutrient or a pair of nutrients. From the results of 23,466 demonstrations it has been found that in 92 per cent of these at least one fertilizer treatment was profitable—even on small, peasant farms at local prices and the average value/cost ratio of the best treatment was 3.7. This implies a profit of 270 per cent on the money spent on the most efficient fertilizer treatment. In the results of nearly 3,128 simple treatments, 96 per cent showed a profitable return to at least one treatment and the value/cost ratio of the best treatment was 8.4—i.e. 740 per cent return on the cost of the fertilizer.

[*The World of NPKS*, No. 21 (1968), 2]

Tung Oil Coatings for Fertilizers

By coating the fertilizer with tung oil, the rate of its release in the soil may be controlled to reduce the losses due to water-leaching. The fertilizer coated in such a manner could be placed in close contact with seeds or plants, eliminating the present use of fertilizer between rows where some weeds may grow. The inventors claim that coating the fertilizer makes its flow through spreaders easier and eliminates corrosion of application equipment and other equipment with which it comes in contact. They say the coatings also provide a vehicle for incorporating agricultural pesticides intimately with water-soluble fertilizers, and that the coatings allow the application of fertilizer immediately after in conjunction with other agricultural chemicals, such as lime.

Tests conducted by the inventors with prilled urea show that the tung oil coatings can be varied to control the per cent solubles leached from 100 to as little as 12 per cent after the urea has been immersed in water for 100 hours.

Three claims have been made on the tung oil coated fertilizers: (1) a capsule for the controlled release of fertilizer comprising an inner core of water-soluble fertilizer and an outer coating consisting essentially of tung oil; (2) a capsule in accordance with claim 1 wherein the outer coating contains additionally a finely divided oil insoluble mineral selected from the class consisting of sulphur, graphite and mica; and (3) the process for the production of a capsule for the controlled release of fertilizer comprising the following steps: (i) admixing tung oil with a water-soluble fertilizer in a particulate form in the absence of a solvent, and (ii) agitating said admixture in the presence of air until the tung oil forms a dry coating around an amount of the said particulate fertilizer.

U. S. Patent No. 3,321,298, awarded to Verne C. Bidlack and Verne C. Bidlack, Jr., of Jenkintown, Pa.

[*The World of NPKS* No. 21, (1968), 3]

Namrup Fertilizer Factory

The Namrup factory, the fifth unit of FCI Ltd., has started producing urea since Aug. 27, 1968. It has a rated capacity of 45,000 tonnes annually in terms of nitrogen, the end-products being 55,000 tonnes of urea (46% N) and 1,00,000 tonnes of ammonium sulphate. The total estimated cost of the project has been Rs. 21,21,63,000 (inclusive of increase due to devaluation). The foreign exchange component has been met from U.K. credit.

This unit is the first in the country to utilize natural gas (obtained by an 11 mile long pipe line) as the basic raw material. The other raw material is elemental sulphur for production of sulphuric acid. It draws its power requirements of 14 MW from the nearby thermal plant owned by the Assam State Electricity Board at Namrup. Water requirements of 6 million gals/day are met from nearby Dilli river. Its ammonium sulphate plant has been designed by the Planning & Development Division, FCI Ltd.

[FCI News, 6 (6) (1968), 10]

Symposium on Chemicals and Oils from Coal

For the purpose of survey and taking stock of the growing field of petro and carbo chemical synthesis and especially the role of coal in it at present and in future, the Central Fuel Research Institute, Dhanbad (Bihar) is organizing a symposium on Chemicals and Oils from Coal during Nov.-Dec. 1969. The symposium will cover broadly the following: development of carbo-chemicals from coal, coaltar

distillates and benzole including refining, recovery and use; direct conversion of coal to oil and chemicals; chemicals and oil by Fischer-Tropsch synthesis and Oxo-synthesis; catalysis in carbo-chemicals synthesis; production of agricultural chemicals, including fertilizers, soil conditioners, pesticides, insecticides, ion-exchangers, detergents, etc. from coal; production of coal chemicals by oxidation, hydrogenation, nitration, electrochemical reduction, bio-degradation, etc.; new techniques of chemical synthesis, e.g. irradiation, ultra high temperature reaction, microwaves, etc; analytical techniques for evaluation, characterization and identification of coal chemicals. At the opening session a 500 l./day vapour phase heavy oil and tar hydrogenation pilot plant will also be formally commissioned.

The symposium will be divided into the following 3 sessions: I (a) Recovery, refining and synthesis of carbo-chemicals and their techno-economic consideration *vis-a-vis* petrochemicals; (b) agricultural, pharmaceutical and other chemicals from coal and by-products of coal and coal carbonization; II—Synthesis of oil hydrocarbons and chemicals (a) hydrogenation and solvent extraction, (b) F. T. synthesis and (c) Oxo-synthesis (d) catalysis in relation to the above processes; III—(a) Chemicals by direct conversion or degradation of coal by oxidation, nitration, electrochemical reduction, etc., (b) fertilizers, soil conditioners and chemicals by bio-degradation, bio-synthesis, etc.; (c) chemicals by irradiation, ultra high temperature reaction in plasma, microwaves, etc. The papers meant for presentation at the symposium should reach the organizing secretary not later than April 30, 1969. These will be later published in a special symposium number by the Chemical Age of India, Bombay.

News in Brief

World's Largest Ammonia Plant

The largest single-train ammonia plant (1500 s.t.p.d.), using natural gas with a high methane content as raw material, has been built recently at Standard Oil Co's Pascagoula refinery in Mississippi (U.S.A.). The gas is piped from an off-shore field by an 80 mile long pipeline, and after desulphurization, it undergoes 2-stage reforming, using 500 psi in the primary reformer. Even after undergoing shift conversion, Catacarb carbon dioxide removal, methanation and intermediate steam generation, the gas reaches the inlet side of the synthesis gas compressor at about 400 psi. This and also the use of steam turbines to drive the centrifugal air and synthesis gas compressor result in low cost, high efficiency synthesis gas compression. Further savings in compression power are obtained by the use of a radial flow reactor, which operates at an inlet pressure of 3200 psi and an outlet pressure of 3050 psi. Heat is saved by drying the syngas as it enters the ammonia converter. Ammonia produced is handled in liquid form at atmospheric pressure and -28°F distribution being by river barges.

[*Nitrogen*, No. 51, (1968), 34]

Desulphurizing Catalysts

A new desulphurizing catalyst developed by the North Western Gas Board, U.K., is described. This special catalyst enables organic sulphur compounds to be removed from hydrocarbons by contacting the latter in the vapour phase in the presence of water vapour at between 350-500°C. The catalyst comprises uranoso-uranic oxide (U_3O_8) and/or uranium trioxide (UO_3) on a carrier, such as alumina. Total uranium oxide content of the catalyst varies between 5 and 10 per cent. Other carriers suggested are silica, kaolin, magnesium silicate or magnesium, calcium, strontium and barium oxides.

North Western Gas Board: British Patent 699,948.

[*Sulphur* No. 75, (1968), 42]

Indian Standards

Ammonium Sulphate: ISI has revised its first specification for ammonium sulphate (fertilizer grade), which prescribes the requirements and methods of sampling and test of the product. In this version, the limit for pyridine has been dropped and a plea for allowing higher free acidity in the by-product ammonium sulphate has been accepted; changes have been made in the statistical scheme of sampling.

Pesticides: The following draft specifications for pesticides prescribing the requirements and methods of their tests have been prepared: pyrethrum emulsifiable concentrates [Doc. AFCDC6 (675)]; warfarin technical (Doc); thiram water dispersible powder [Doc. AFCDC 6(679)]; thiram seed dressing formulation [Doc. AFCDC6 (680)]; Coumafuryl technical [Doc. AFCDC6(683)]; gamma BHC (Lindane) smoke generators [Doc. AFCDC 6(701)].

[*Chem. Age of India*, 19 (1968), 467 & 468]

New Rice Variety From Philippines

The International Rice Research Institute at Los Baños, Philippines has announced the development of a new rice variety I.R.8. This variety, evolved from a cross between Peta a tail Philippines variety originating in Indonesia and a shorter variety called Dea-ges-woo-gen from Taiwan, could yield 10-16 tonnes per hectare and could be grown during any season in the tropics and has a maturing period of 120-130 days. Because of its immediate response to nitrogen fertilizers, the new variety is also disease-resistant. Furthermore, it has a high swelling coefficient and cook dry and fluffy. Many countries are switching over to the new variety on an experimental basis.

[*Science J.*, 4 (5) (1968), 29]

Urea for De-icing Runways

Urea is now being used across Canada to help runways and landing areas of civil and military airports clear of ice and snow.

[*Nitrogen*, No. 52, (1968)]

Reduction of Pressure Drop in NH₃ Plant Shift Converter

In an ammonia plant producing synthesis gas with reformers, a pressure drop problem was encountered in the shift converter due to carry-over of catalyst dust from the secondary reformer. To avoid the method whereby this dust is removed by shutting down, the catalyst is oxidized, the converter is entered and the dust removed from the top of the catalyst beds by vacuum cleaning. An alternative method has been tried at Nipak Inc.'s plant at Pryor, Okla. The method, which proved very successful, reduced the pressure drop by 24 psi. (38 to 14 psi). It consisted of the following steps: the secondary reformer was blocked from the shift converter and vented to the atmosphere. Then, when the shift converter also had been blocked in, hot and depressurized, 275 psi. steam, was introduced at its bottom, until full pressure had been reached in the vessel. At this time, the 4 in. vent to the atmosphere on top of the shift converter was opened rapidly and completely, and then depressurized very quickly to a low pressure. This was repeated several times, or until no dust was observed coming out of the vent.

The shift converter has been kept in optimum condition by repeating the procedure many times since it was first started. When the converter catalyst was changed long after this method was adopted no damage was observed. Lost production time has been reduced to a minimum, and maintenance work completely eliminated. The producer of the catalyst has shown great interest in the procedure.

W. (Bill) Sisson, Nipak, Inc., Pryor, Okla, Chem. Eng. 1967, 23 October (200).

[*Nitrogen*, No. 52, (1968),]

Low-temperature Fertilizer Granulation Using Anhydrous Ammonia

Use of anhydrous ammonia for the liquid phase of granulation instead of water is noted in a recent British Patent (Pat. No. 1, 083, 081, 1967).

To the solids to be granulated are added
(a) a solution or slurry containing at

least 60 per cent of ammonium nitrate in liquid ammonia or (b) liquid ammonia to the solids which already contain ammonium nitrate. Evaporation of the liquid ammonia (which is recovered) produces hard granules. The operational temperature is between -10° and 40°C. At lower temperatures the bonding action is too weak, and the ammonium nitrate separates as a powder. At higher temperatures there is a rapid evolution of ammonia causing breakdown of the granules.

The advantage of this process is that it can be carried out at temperatures well below the thermal decomposition point.

[*Nitrogen* No. 52, (1968), p. 38]

Sulphuric Acid from Phosphoric Acid Gypsum

In a recent full-scale demonstration at VEB Chemiewerk, Coswig (E. Germany), the gypsum that is produced during the manufacture of phosphoric acid was utilized to produce sulphuric acid. In a process similar to the Mueller-Kuhne process, the gypsum is dried and calcined in a rotary drum, mixed with coke, sand, clay and roasting residues consisting mainly of Fe_2O_3 , then fed to an oil- or coal-fired rotary kiln. At a temperature of just over 1400°C, the gypsum decomposes, giving off sulphur dioxide and leaving a residue that emerges from the kiln in the form of a clinker which is cooled, ground and used as the basis for cement. The sulphur dioxide passes to a conventional gas-cleaning and contact plant where sulphuric acid is produced.

At present, there are no wet process phosphoric acid plants in East Germany, but the construction of a unit of significant size is planned at Coswig in the near future, and it is expected that this new process will be used to enable the phosphoric acid plant to be virtually independent of external sulphur sources, as the sulphuric acid produced would be recycled to the phosphoric acid unit.

The gypsum process has been developed to the stage where VEB Chemie-Ingenieurbau of Leipzig is prepared to design and engineer a plant with a single stream capacity of up to 300 t.p.d. H_2SO_4 .

Dehydration of Solutions of Hygroscopic Materials

Experimental work using a fluidized-bed technique for the dehydration of several materials, including ammonium sulphate and trisodium phosphates, has recently

been carried out in the U.S.S.R.* The interesting features of the experiments are the utilization of gases at temperatures above the melting point of the material being treated, used in conjunction with a novel nozzle feed arrangement at the base of the bed.

The fluidized bed is first loaded with solid crystalline material, and cold air from a cold air chamber surrounding heat exchanger nozzles is blown in upwards through the support grid to set the bed in motion. The solution to be dehydrated is fed under pressure to the liquid feeder nozzles and at the same time, hot flue gases are passed through the heat exchanger nozzles in such a manner that the flows combine. Flash vaporization occurs immediately prior to the point of entry into the bed, and on entering the bed, the melt crystallizes on contact with the cold air fluidized crystals already present. Product is withdrawn through a central discharge pipe, the rate being controlled by the upward flow of air through the pipe.

*Groshev G. L. et al., Khim, Prom., 1967, (6), 56.

[*Phosphorus and Potassium*, No. 33, (1968), 48]

Synthesis Gas

A new process for making synthesis gas involves the production of hydrogen by cracking hydrocarbons in the presence of oxygen and subsequently cracking it with liquid nitrogen. It can be operated successfully using two rectification columns for liquefying and rectifying air to provide the nitrogen, the columns being operated under reduced pressure and in thermal contact with each other. The arrangement allows a portion of nitrogen gas at the head of the first rectification column (at high pressure) to be condensed by heat exchange with a liquid having a high oxygen content, which is separated in the second rectification column, the latter operating at a lower pressure. The efficiency can be improved by condensing part of gaseous nitrogen which separates at the head of the first column by heat exchange with liquid nitrogen. The condensed nitrogen can then be rectified.

[*Res. & Indus.*, 13 (1) (1968), 34]

Concentrated Phosphoric Acid

A new process for manufacturing cheaper and more concentrated phosphoric acid has been developed by a British firm. It produces acid upto 50 per cent P_2O_5 without the need for evaporation. Based on the

separation of the hemi-hydrate of calcium sulphate by a single filtration stage, the process has many advantages, viz. a more concentrated product, several stages of manufacture are eliminated and a coarser rock can be used. Under the correct operating conditions, the hemi-hydrate product is fast filtering and can be washed economically. The number of wash stages is usually three or four. The stability of the crystals is such that there is no danger of gypsum forming either in the reacting system or on the filter during washing.

[*Chem. Age of India*, 19 (1968), 476]

Pakistan's Fertilizer Project

Pakistan's fourth fertilizer project, promoted by Hyesons Agricultural Chemicals group and to be sited at Mirpur Matelo in the Indus Valley, will use Toyo Koatsu total recycle urea process for its 363,000 tons/yr urea unit and the Kellogg ammonia synthesis process for its 198,000 ton/yr ammonia unit.

[*ibid*]

Urea Nitrate and Urea Phosphate as Fertilizers for Grass and Barley

At low levels similar amounts of nitrogen were recovered, in glasshouse pot trials with grass, from urea nitrate (I) and ammonium nitrate (II) applied to a sandy loam and a clay loam, although at high applications the early growth was damaged by I. In the field, herbage was scorched by I, and I at 200 lb/acre produced less dry matter than did II. I-urea phosphate, (III), and a III-urea mixture were compared with II for barley and grass. On a light soil growth was least good with I. III and the mixture were superior to II. Whilst HNO_3 , due to its mobility in the soil, was ineffective in absorbing the free NH_3 from the hydrolysis of urea, H_3PO_4 because of its lower mobility allowed the urea to diffuse into a larger volume of soil before hydrolysing and was still present to absorb the free NH_3 formed. I and III have good physical forms and III has promise for mixed NP and NPK fertilizers.

[*The World of NPKS*, No. 22, (1968)]

Sulphur for Control of Tuber Disease in Potatoes

Trials in Northern Ireland have shown that the application of sulphur to the soil before planting has substantially reduced the incidence of tuber disease, such as common scab, powdery scab, black scurf and blight. It is noted, however, that there is no standard rate of application,

treatment is expensive, precautions must be taken during application and sulphur makes the soil acid.

[*The World of NPKS*, No. 22, (1968)]

Gypsum Treatment for Saline Soil in U.S.S.R.

Gypsum has been employed successfully in desalting the soil in Kirghizia. The gypsum is applied during winter following the amount required depending on the content of sodium salts in the soil and the absorption capacity of the earth. Application rates vary from 2-8 tonnes/hr, and can rise to 15-25 tons for extremely saline soil.

[*The World of NPKS*, No. 22, (1968), 30]

Behaviour of Urea and Nitrophosphates (PEC and ODDA) Under Storage Conditions

The behaviour of urea packed in alkathene liners with jute over-bags and nitrophosphates (PEC & ODDA), packed in crepe paper-lined jute bags, under storage conditions is reported. With increasing time lump formation also increased, urea showing lesser tendency to lump. The moisture absorption by the fertilizers was very low in case of urea but high for PEC nitrophosphate. It was seen to be a function of temperature and humidity. The nitrogen reduced with time of storage, PEC product showing greater loss. There was an apparent gain in P_2O_5 content of nitrophosphates with time of storage.

Source: J. Indian Soc. of Soil Sci. 1967, Vol. 15, No. 2.

[*The World of NPKS*, No. 21, (1968), 26]

Phosphorus Pentoxide in Phosphate Fertilizers

The methods investigated for determining P_2O_5 were—(i) pptn. of the P_2O_5 as molybdophosphate or $MgNH_4PO_4$; (ii) titration after pptn. as quinoline molyb-dophosphate, complexometric titration, or titration with alkali in the presence of $CaCl_2$; and (iii) colorimetry as reduced molyb-dophosphate or as molybdoavanado-phosphate. The effects of foreign ions were investigated. A first pptn. as molyb-dophosphate, secondary pptn. as $MgNH_4PO_4$ and conversion into $Mg_2P_2O_7$ is sufficiently accurate, even in the presence of foreign ions, to be used as a reference method. Direct pptn. and weighting as molyb-dophosphate, pptn. as $MgNH_4PO_4$ in the presence of citric acid, and (for up to 30% of P_2O_5) calorimetry as molybdo-avanadophosphate are also generally satisfactory.

Source: Weiser, H., and Riedel, V. (WTZ Schwefelsaure u. Phosphatdungsmittel Heinrichshall, Bad Koschitz, Germany). Chem. Tech. Berl., 1966, 18 (9), 561-564.

[*The World of NPKS*, No. 23, (1968), 31]

Fire Hazards of Ammonium Nitrate-Sulphur Systems

The addition of sulphur to ammonium nitrate-based fertilizers has raised questions regarding the hazard of these mixtures when exposed to fire. Several techniques were used to evaluate this hazard. Ammonium nitrate-sulphur (AN-S) mixtures, of sufficiently large diameter, deto-

nated when initiated by an explosive shock. Diammonium phosphate, triple superphosphate, and potassium chloride added to AN-S mixtures decreased the shock sensitivity relative to AN-S. AN-S mixtures burning at pressures greater than 1,000 p.s.i. resulted in rapid combustion; deflagration to detonation transition was accomplished experimentally in some cases. Sulphur has the same effect on detonability as other fuels when added to AN or AN systems. The thermal stability of AN-S mixtures was about the same as AN mixed with fuel oil or polyethylene. Addition of chloride ion materially reduced the thermal stability.

Mason, Charles M., Forshey, David R., and Perzak, Frank J. P.

[*The World of NPKS*, No. 23, (1968)]

Results of Fertilizer Tests with High Basic Slag Applications

To improve the nutrient and reaction ratios of newly cultivated poor soils, extensive fertilizer tests showed that fertilization with high basic slag application was very successful. With quantities of up to 6,700 kg/ha basic slag, high increases in yield were obtained which made the expenditure on fertilizer highly economical, and confirmed that heavy basic slag fertilization is to be highly recommended.

Source: Pilaski, Dr. W., Walden, O. (Oldenburg, I.O.). Die Phosphorsaure, 1967, 27, (1/2), 79-87.

[*The World of NPKS*, No. 23, (1968), 30]

STATISTICS

TABLE 1—DOMESTIC PRICES OF FERTILIZERS IN DIFFERENT COUNTRIES

U.S.A.		U.K.		WEST GERMANY	
Fertilizers	Prices	Fertilizers	Prices	Fertilizers	Prices
(January 1968)		(Jan.-Feb. 1968)		(Jan. -Feb. 1968)	
Ammonia, anhydrous					
Fertilizer grade	\$84.00-\$92.00 per s. ton	Ammonium sulphate (21% N)	21 5 0 6 4 3	DM per 100 kg. delivered in bulk, in 25-tonne lots	
	cars, delivered	Nitro-chalk (21% N)	22 16 0 6 4 3	Ammonium sulphate nitrate (26% N)	26.78
Refrigeration grade	\$86.50 per s. ton	Nitro-Shell (26% N)	28 4 0 7 13 10	Ammonium sulphate (21% N)	21.63
	cars, delivered	"Nitram" (34.5% N)	34 5 6 10 4 1	Calcium ammonium nitrate (23% N)	23.69
Ammonium Sulphate (21% N)				Urea* (46% N)	46.46
Standard granular	\$31.00 per s. ton			Calcium nitrate* (15.5% N)	20.31
	bulk, f.o.b. plant				
Large granular	\$33.00 per s. ton	Compound Fertilizers:		*In bags.	
	bulk, f.o.b. plant	(N-P ₂ O ₅ -K ₂ O)		*In bags.	
Nitrogen Solutions		Fisons High N-52	20-10-10 37 2 6 8 4 2		
Manufacturing	\$1.30 per unit, s. tons,	Fisons High K-51	13-13-20 36 12 0 6 17 0		
	cars, f.o.b. plant	ICI No. 2	22-11-11 40 18 0 9 0 9		
Direct application	\$1.30 per unit, s. tons,	ICI No. 1	12-12-18 33 10 6 6 5 8		
	cars, f.o.b. plant	Shell No. 5	23-10-11 41 3 0 9 2 10		
Urea		Shell No. 4	15-15-23 42 5 0 7 18 10		
Fertilizer grade (45% N)	\$82.00-\$86.00 s. ton bulk,				
	delivered				
Fertilizer grade (46% N)	\$84.00 s. ton bulk,	*EDR: January 10s.			
	delivered				
Industrial grade (46% N)	\$94.00 s. ton bags,				
	delivered				
Ammonium nitrate (33.5% N)	\$62.50 s. ton bags, f.o.b.				
	plant				

NETHERLANDS		FRANCE		ITALY	
Fertilizers	Prices	Fertilizers	Prices	Fertilizers	Prices
D. F. per 100 kg. delivered in bulk, min. 80-tonne lots		Fr. per 100 kg. delivered in bulk, min. 20-tonne lots, railway		L. per 100 kg. delivered in plastic sacks, incl. tax (price to distributors)	
CAN	23% N	1968		January/ February, 1968)	
"Magnesamon"*	20% N	January	February		
Calcium Nitrate*	15.5% N	17.10	17.50	Ammonium sulphate 21% N	28.96
Ammonium sulphate 21% N		19.10	19.50	Urea (Perlurea) 46% N	55.45
*In bags.		14.60	15.00	CAN (Ammonitrate)	
		16.50	16.50	22% N	27.29
				26% N	31.63
				33.5% N	39.95
				Calcium Nitrate 15.5% N	26.49
				Ammonium Nitrate 34.8% N	40.30

NORWAY		BELGIUM	
Norw. Kr. per 100 kg. in bags, fob, plant		B. Fr. per 100 kg. delivered in bulk, min. 20-tonne lots (excl. tax)	Feb. '68
Calcium ammonium nitrate	26% N	Feb. '68	
Calcium nitrate	15.5% N	32.80	224
Urea	46% N	20.30	256
		61.70	277
			255
			465

*Min. 10-tonne lots.

Exchange Rate: 1 U.S. Dollar = 0.417 Pound = 4000 Franc = 624,830 Lira = 4000 DM = 49630 Belgium Franc = 3603 D. Florin = 7140 Kr.

[Nitrogen, No. 51, (1968). 4]

TABLE 2—WORLD FERTILIZER NITROGEN BALANCE

	('000 metric tons N)			
	1966/67	1967/68		
	Production	Consumption	Production	Consumption
Western Europe	6,777	5,018	7,296	5,262
Eastern Europe	4,730	4,711	5,561	5,491
North America	6,096	5,697	6,740	6,365
Central America	289	546	324	589
South America	223	253	247	283
Africa	243	555	315	647
Asia	3,502	4,698	4,035	5,420
Oceania	39	99	45	108
WORLD	21,899	21,577	24,581	24,165
Less Losses*	21,571	—	24,212	—

*An estimated 1.5% of production is lost between factory and farm each year, in bagging, distribution and compounding.

[Search, 5 (4) (1968), 204]

TABLE 3—PLAN OUTLAY & AGRICULTURAL PRODUCTION IN INDIA

[Targets for 1968-69]

I. Plan Outlay

Item	1967-68		1968-69
	Outlay	Expenditure	Outlay
in crores of rupees			
Agriculture	306.65	284.87	270.24
Community Development & Cooperation	69.85	70.02	57.54
Irrigation (including Flood Control)	146.77	147.16	154.69
Power	384.78	400.56	338.80
Organized Industry	520.19	520.85	539.33
Village & Small Industries	43.55	44.94	41.41
Transport & Communications	418.76	424.09	426.16
Education	111.66	113.82	120.46
Scientific Research	19.06	18.20	22.03
Health & Family Planning	75.84	73.94	88.80
Water Supply	36.96	36.86	33.81
Housing & Urban Development	25.87	27.00	22.98
Welfare of Backward Classes	17.73	20.06	20.02
Social Welfare	4.43	4.50	4.73
Craftsman Training & Labour Welfare	15.31	13.64	13.73
Public Co-operation	0.59	0.38	0.48
Rehabilitation	16.08	13.46	14.65
Rural works	6.50	6.50	4.50
Other programmes	25.49	29.25	21.85
Buffer Stocks	—	—	140.00
Total	2,246.07	2,242.10	2,337.21

II. Agricultural Production Targets, m. tonnes

Foodgrains	102.00
Sugarcane (gur)	12.50
Oilseeds	10.00
Cotton	6.70
Jute	6.90

[FAI Inf. Serv., 9 (14), (1968), 8]

TABLE 4—WORLD NITROGEN FERTILIZER PRODUCTION

	Nitrogen Fertilizer Production (in 1,000 tonnes N)			Nitrogen Fertilizer Consumption (in 1,000 tonnes N)		
	1965-66	1970-71	1975-76	1965-66	1970-71	1975-76
United States	5,160	7,500	10,000	4,820	6,700	9,200
Canada	375	700	1,100	220	500	800
Western Europe	6,300	8,500	10,500	4,625	6,500	9,000
Japan	1,615	2,000	2,400	775	900	1,000
India	235	850	2,000	585	1,500	3,000
Rest of Asia	400	1,000	2,000	900	1,500	2,500
Africa	235	800	1,600	655	1,200	2,000
Latin America	520	750	1,100	675	1,000	1,500
Australia	35	200	300	85	200	300
U.S.S.R.	2,710	6,000	10,000	2,280	5,500	9,200
Eastern Europe	1,615	3,500	6,000	1,890	3,500	5,500
Communist Asia	600	1,200	2,200	1,165	2,200	3,300
World Total	19,800	33,000	49,000	18,675	31,000	47,000
Production and consumption, non-fertilizer uses of N	3,400	6,600	10,000	3,400	6,000	10,000
Production and consumption, total	23,200	39,000	59,000	22,100	37,000	57,000

Source: Dr. Raymond Ewell.

[The World of NPKS, No. 23, (1968), 14]

TABLE 5—NON-COMMUNIST WORLD PRODUCTION AND CONSUMPTION OF SULPHUR IN ALL FORMS

(1,000 Long Tons)

Year	Elemental	Production Non-Elemental	Total	Elemental	Consumption Non-Elemental	Total	Production, Surplus or Deficit
1956	8,684	8,872	17,556	7,824	8,475	16,299	1,257
1957	8,227	9,016	17,243	7,606	8,480	16,086	1,157
1958	7,718	8,886	16,604	7,469	8,398	15,867	737
1959	8,211	8,662	16,873	8,573	8,275	16,848	25
1960	9,229	9,975	18,204	9,217	8,491	17,708	496
1961	10,104	8,850	18,954	9,162	8,754	17,916	1,038
1962	10,577	8,851	19,428	9,688	8,611	18,299	1,129
1963	10,913	8,424	19,337	11,050	8,440	19,490	-53
1964	11,931	8,891	20,822	12,833	8,943	21,776	-954
1965	13,076	9,265	22,341	14,339	8,976	23,315	-974
1966	14,284	9,800	24,084	15,116	9,900	25,016	-932

ANNUAL % GROWTH

1956	14.3	10.4	12.3	6.1	5.4	5.7	
1957	- 5.3	1.6	- 1.8	- 2.2	0.1	- 1.3	
1958	- 6.2	- 1.5	- 3.7	- 1.8	- 0.1	- 1.4	
1959	6.4	- 2.6	1.6	14.8	- 1.6	6.2	
1960	12.4	3.6	7.9	7.5	2.6	5.1	
1961	9.5	- 1.4	4.1	- 0.6	3.1	1.2	
1962	4.7	0.01	2.5	5.7	- 1.6	2.1	
1963	3.2	- 4.8	- 0.5	14.1	- 2.1	6.5	
1964	12.8	5.5	8.0	16.1	6.0	11.7	
1965	9.6	4.2	7.3	11.7	0.4	7.1	
1966	9.2	5.8	7.8	5.4	10.3	7.3	

[Proc. of the 17th Annual Meeting, Fertilizer Industry Round Table 1967 USA, p. 46]

TOWARDS SELF-SUFFICIENCY IN CATALYSTS

Because of delay in the receipt of the imported catalysts during the commissioning of the Namrup Unit of FCI Ltd., a number of catalysts, viz. those meant for steam-natural gas reformation, secondary gas reformation, primary and secondary high temperature CO-conversion, developed and prepared at the Planning & Development Division, were delivered at a short notice, which eventually saved the delay of the start-up of the factory and consequently loss of production. Apart from self-sufficiency, the charging of these catalysts has saved the country's foreign exchange to the extent of Rs. 4.00 lakhs. The performance of these catalysts has been well up the mark. In this case, the significance is that the entire stream upto CO-conversion is being operated using indigenous catalysts.

Besides the above, this Division is capable of supplying many other catalysts required in the manufacture of ammonia. There are hardly a few manufacturers in the world who have their own know-how for the manufacture of the type of catalysts used in the Namrup plant recently. A number of catalysts developed in this Division have been in commercial use in the FCI's Sindri Unit for the last several years and a few of these have now been supplied to the public and private sector fertilizer plants.